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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

GODDARD SPACE FLIGHT CENTER

1973 GSFC BATTERY WORKSHOP

FIRST DAY

Room 205
Building 26,
Goddard Space Flight Center
Greenbelt, Md.

Tuesday, 13 November, 1973

Tom Hennigan,
Chairman, Morning Session

Floyd Ford,
Chairman, Afternoon Session

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P R O C E E D I N G S

HENNIGAN: We had a little delay this morning but we'll try to start off here and our guest speaker will be here in a few minutes.

I'd like to welcome you all to Goddard Space Flight Center and the 1973 Goddard Battery Workshop. A full two-day meeting is planned including seals, separators, manufacturing processes and improvements, test results and a final session tomorrow afternoon on improved energy-density system or the metal-gas, metal-hydrogen system.

The plans call for seals and separators this morning and storage experience and manufacturing developments this afternoon. We may be a little short this morning, so the manufacturing and storage experience might creep into the latter part of the morning.

Now, as in the past, we encourage active participation. Although papers are prepared, your comments and discussions are solicited. And feel free to come up and use any of the chalkboard or the charts, if you feel a sketch will help you in your discussion of the topic being taken up at the time.

We are happy again to welcome fellow visitors from Canada, France, Germany and the Netherlands.

I will chair the first session today on seals and separators, while Floyd Ford will chair the afternoon session on storage experience and manufacturing developments.

As you plan to give a paper or a discussion of these topics, please contact either one of us. We hope your meeting will be very interesting and informative.

While we're waiting for our speaker, I'll just make a few announcements that we had. If you have any questions on travel, the extension to call here is 2221, and they'll try to help you out. I would appreciate it very much if you'd purchase the tickets for the cocktail party before noon. We have to have a count by noon and this afternoon the price might go up due to inflation.

(Laughter.)

To the speakers: please bring copies of your slides and viewgraphs to the chairman of the session as you come up to the podium. And when making questions from the floor or any discussions from the floor, please state your name very clearly for the recorder and what your affiliation.

As you know, the entire proceedings are recorded. They are also taped and this is put into our proceedings which we usually try to get out to you within a month or so, six weeks I suppose. And it's unedited and besides that, if we had edited it, I think it would be a long time before you got it.

Oh, one thing, I'd like to pass around a couple of pads here for you people to put your attendance and your company address. Then we will use these for the mailing list for our proceedings. I was hoping -- the time is just right -- he'd got the doors open and he'd come in. Oh, okay, I didn't see you, fine.

At this time, we have a special guest, Mr. Don Hearth, who is Deputy Director of Goddard Space Flight Center. I would like to present Mr. Hearth, who has some words to say with regards to the workshop, batteries, and what the future holds.

Mr. Hearth?

HEARTH: I was sitting right out in front of Tom, so I guess he didn't see me.

I'd like to welcome you to the Center today and to the 1973 Workshop on Batteries. As in the past five years, Goddard has sponsored this workshop in order to insure a review of current battery technology so that the application of this technology could be spread amongst all of the users and providers of this technology.

I think any of us involved in technological activities recognize that with the rapid changes in any technology that information exchange is very important. I know from a personal point of view, I know I certainly wouldn't want to go out and design an airplane today. I'd have a little bit of trouble.

So, certainly in the area of power systems, there is need for information exchange. And we have found that this type of workshop, that is, an informal exchange of information,

has well served that purpose. And we hope that the meeting during the next two days will assist Goddard, will assist other NASA Centers, or assist DOD and its agencies, people from overseas, as well as industry, in providing the most recent exchange of experiences and technology in the battery area.

For the last thirteen years since 1960, this Center has pursued an active part in research and development and testing of batteries for spacecraft. There have been many results of these efforts. They include the non-magnetic silver/cadmium battery, the third electrode, the recombination electrode, an increase in the depth of discharge from a few percent to 25 percent and so forth.

There has been one area during, excuse me, during this experience that requires continued emphasis, that is, the area of assuring a high-reliability, uniform product from lot to lot and year to year.

This requirement was recognized during the mid 1960s, when production problems kept reoccurring in the manufacture of non-magnetic cells. And during 1967, several problems occurred in the production of nickel/cadmium cells and initiated the development of a process and material control spec for the manufacture of these cells.

In this area, participation of a number of people, I'm sure who are here today and previous workshop meetings, have been most helpful in developing this spec, not only for NASA and Goddard but for battery users in the military, commercial and specialized fields.

Present spacecraft designs and studies are underway for missions well into the 1980s. These missions will continue to require batteries, particularly nickel/cadmium batteries as the primary energy storage device. There are, however, two tasks that are presently receiving increasing attention within that, so that I'd like to mention this morning.

In general, they relate to spacecraft components across the board, but in the case of batteries, they include two. First, there's the standardization of batteries at the cell level and at the battery level. And secondly, there's the standardization of the testing of batteries, in particular, the need for the development of an accelerated test for both cells and batteries.

Now, both of these areas are tied to a concerted effort on our part to reduce the cost of doing business. And, I know this is a familiar tune that has been played for many years, but I think there has been a change in the past few years within our agency at least, in recognizing that we have reached that stage in the space program where we are in a position to reduce substantially our cost of doing business because we now have better understanding of how to do things in space.

I think the major technical challenges are no longer in spacecraft, as such, but are rather in the experiments and in the sensors to be flown by these spacecraft. I think what this means is that engineers and I think I qualify to be one of those, no longer can reinvent the wheel. Rather what we need to do is to apply our ingenuity and our energies into finding ways to reduce cost because, clearly, there is much more we can do from space than resources will permit.

And the cheaper we can make our missions, then the more that can be done and the greater contribution that those of us involved in space can make to society in general. And I think that's true in the area of batteries as well.

Now, a recent NASA study has shown that all missions, with the advent of the Shuttle, can be accomplished with four basic sizes of nickel/cadmium cells, rather than the 30 or more that have been used in the past and that ties into the need for standardization.

In addition, the development of an accelerated test program, which could reduce years of testings to a few months, we view as mandatory, if cost of spacecraft batteries are, in fact, to be reduced.

I think that the clock is ticking on this problem and I would hope that those of you here today will take back when you go back home, a feeling that we really must solve this problem. And I think that if we all put our shoulders to the wheel we will.

In a way, it reminds me of a story I heard which is supposed to be true of Winston Churchill, who was being introduced at a -- this was after he was knighted and shortly near the end of his career -- he was being introduced to a university audience in England by the University President or Chancellor, or whatever. And this particular individual felt that whenever he introduced the speaker, he really should not just talk about all the good things about the speaker, but really

needed to talk about, you know, the whole man. And this particular individual had always been troubled by Winston Churchill's drinking habits and so he felt that he simply had to mention that.

So, in any event, as he was introducing that gentleman, he pointed out to the audience that he had computed that in Winston Churchill's lifetime he would drink sufficient brandy to fill the auditorium to the floor to the first railing of the balcony.

And, then he proceeded to go on and introduce Winston Churchill. And Churchill got up, and of course you know he had a great sense of humor and the first thing he did was to stand at the podium like this and look down at the floor and then look up at that railing and said, "So much to do in so little time."

(Laughter.)

And, I think that's our problem here -- that we've got a lot to do and we really have very little time to do it and I hope that this meeting will help that problem. And we're glad to have you again and hope you have a very productive meeting. Thank you very much.

(Applause.)

HENNIGAN: Thank you very much, Mr. Hearsh, for your welcoming address. We'll start off with the meeting this morning and we have two speakers on seal developments during the last year or so. Our first speaker is Steve Gaston, from Grumman's Aircraft, who has a presentation on large ceramic seals for nickel/cadmium cells.

GASTON: Good morning. The topic of my little presentation is large ceramic terminal seal progress. I'd like to present a short report on the progress made by Grumman on large ceramic terminal seals since our last discussion on this subject in the 1971 Workshop.

At that time, we were presented with evidence showing a weakness in some of the large-size ceramic seal terminals, which could, and in some instances, did give rise to cracking in the ceramic body with a resultant leakage through the seal.

All work presented here was conducted under the 100 Amp Hour Battery Development Program for large manned space stations on the contract NAS-911074.

(Slide 1.)

Slide 1 shows the negative terminal of one of these early 100 Amp Hour Development Cells. It was constructed in Spring, 1971. Hairline cracks in the ceramic under the brace joint and voids in the brace were observed. These cracks centered around the outer diameter of the ceramic sleeve but did not extend to the inner diameter, thus, a leakage path from the cell's interior to the exterior was avoided.

However, the joint integrity was questionable due to this condition. Specifically, I'm talking about this area right here. This one is 100 times enlarged; you see it here.

(Slide 2.)

Slide 2 shows the positive terminal of the same cell and essentially the same defect as the negative terminal, possibly you see a little bit more pronounced on this one right there.

The first steps to resolve this potential problem were taken by Grumman, Eagle Picher, and Ceramaseal at the 1971 Workshop and are shown in Slide 3.

(Slide 3.)

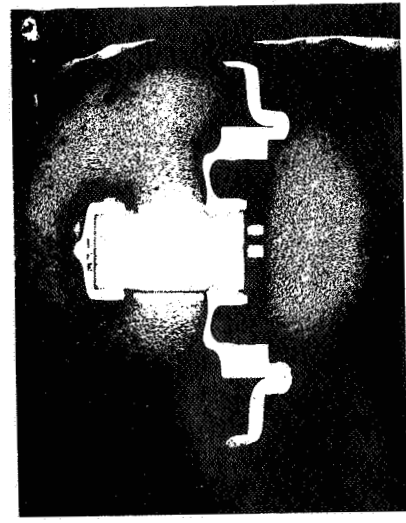
These are essentially the items which we thought are most important and need modification, consists of the increase in purity level, elimination of surface, which is the silica which is potentially attacked by the KOH and possibly a problem, the change in the retainer material to 52 percent nickel alloy, the 42 percent alloy needs a copper plating, which was considered undesirable, and most essential, the type of component tolerance, to get a better braze flow. Of course, the greater control of the braze material and the application of the Q-A provisions as they were developed under the Process Variable Study under NAS-521159.

We also took a close look at possible alternate suppliers, such as G.E., Hughes and Bell's Ziegler seal. Since a terminal of this size was not one of their off-the-shelf items and evaluation of any of these would have been too costly to this austere program.

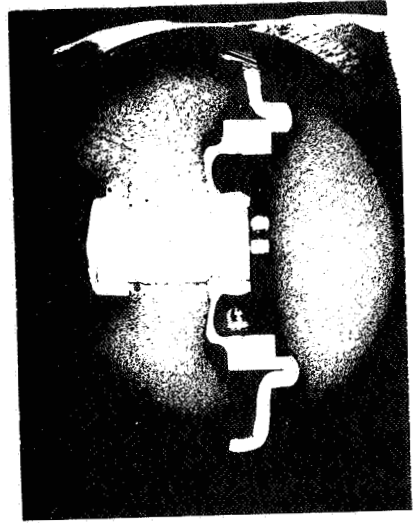
In May, 1972, we received sample terminals with 99.5 and 96 percent aluminum ceramics. They were examined and we found good braze joints, but fine hairline cracks. The cracks in the 96 percent aluminum were shorter. There was no cause to question the seal integrity of this terminal with a 96 percent aluminum and it was used for the construction of the parametric

SN 14

SN 14



2 x



2 x



100 x



100 x



NEGATIVE TERMINAL

POSITIVE TERMINAL

FIGURE 1

FIGURE 2

cell group of the 100 Amp Hour Battery Program.

Shortly after construction completion of these cells, leakage in some of them was observed, showing that this problem was not fully resolved. In October, 1972, it became apparent that further efforts on this terminal design would be unsuccessful in resolving its inherent problem.

Consequently, a newly developed ceramic seal butt seal terminal was examined more closely. A sample cover was received at Grumman in November, 1972. It was metallurgically examined and it is shown in Slide 4.

(Slide 4.)

This terminal is actually upside down. That is the top flag. We modified it from the original platform. This is a top flag and this is -- you're looking at the bottom -- this is the butt seals. These are enlargements of this joint.

From this and other tests we conclude that this terminal looks superior to those previously supplied. Some improvements were suggested, such as, better braze flow control, since material float towards the perimeter, leaving less material near the inner diameter and better cleaning of the bottom well to cover.

Essentially, you see here the brazes tend to float to the outside. Grumman applied a radiographic examination on this sample which is shown on Slide 5.

(Slide 5a.)

One can note that void areas in the braze can be detected with this non-destructive technique. The top view shows two voids, the bottom view shows that these voids are located in the top cup seal. I guess you can detect in here.

(Slide 5b.)

This is a viewgraph made from the x-ray and it's not quite as, the contrast is not quite as big as the x-ray had shown. These are the two voids and if you take a close look, you can see the corresponding voids at the top cup.

The Ceramaseal butt seal was subsequently used on the life test and last group of cells on a 100 Amp Hour Development Program. The design utilized the improvements that are shown in Slide 3, except the increase in aluminum purity to 99.5 percent. 96 percent purity was found to be adequate.

LARGE CERAMIC TERMINAL

SEAL IMPROVEMENT STEPS

NOVEMBER 1971

- INCREASE IN ALUMINA PURITY LEVEL TO 99.5% MINIMUM
- ELIMINATION OF SURFACE GLAZE ON THE CERAMIC
- CHANGE IN RETAINER MATERIAL TO 52% NICKEL ALLOY
- TIGHTER COMPONENT TOLERANCES
- GREATER CONTROL OF BRAZE MATERIAL
- APPLICATION OF Q.A. PROVISIONS
(AS DEVELOPED UNDER NAS 5-21159)

FIGURE 3

GRUMMAN AEROSPACE CORPORATION
Dec 12 1972

FIGURE 4

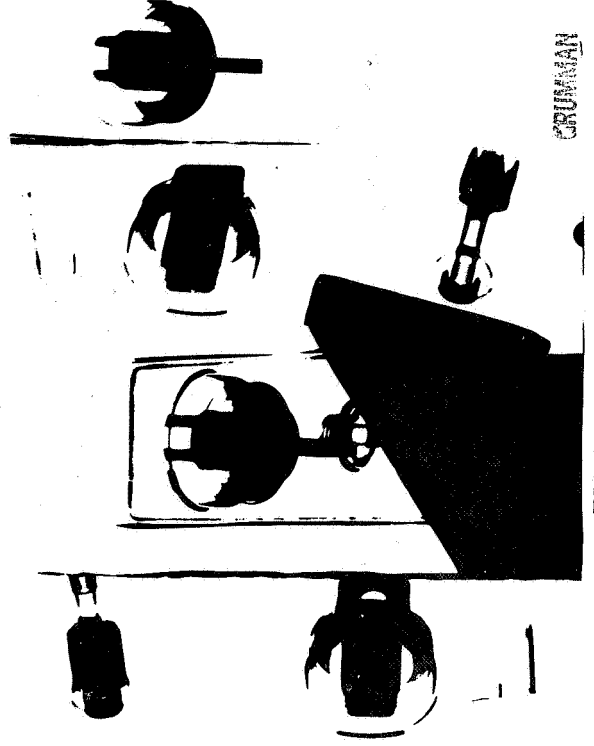
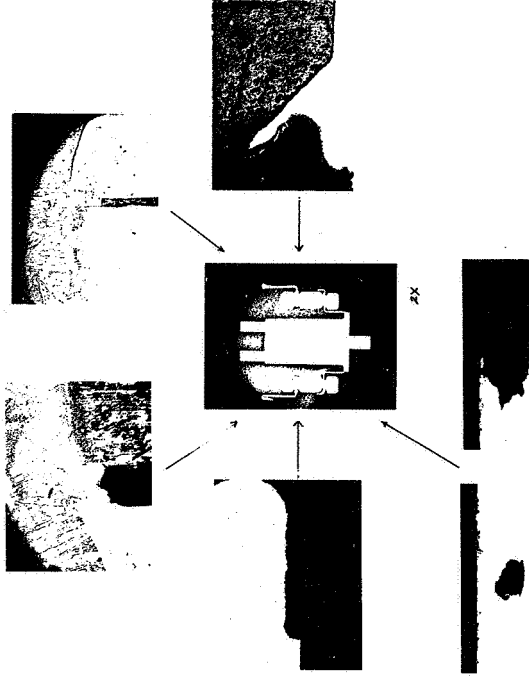
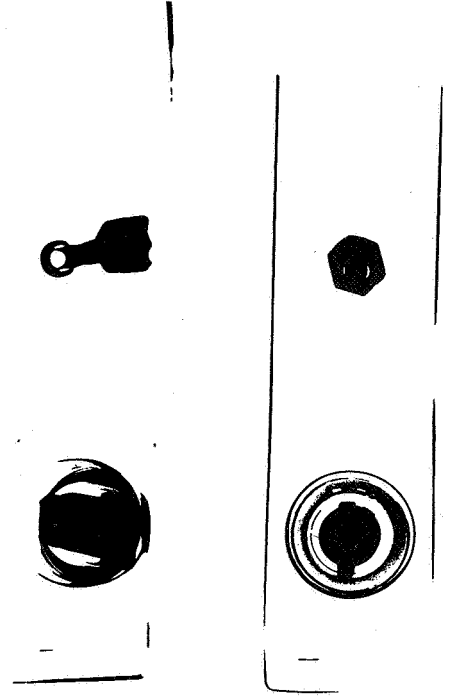


FIGURE 5B

FIGURE 5A



GRUMMAN

9a

Every cover used received a top-view radiographic examination. A typical sample is shown in Slide 6.

(Slide 6.)

All of these covers have been constructed without leak problems and many of them will be shipped to N.A.D. Crane for testing. In conclusion, I would like to say that the radiographic examination of terminal seals has added an important, non-destructive tool to insure a better quality terminal. It is applied best prior to the terminal weld to cover, since it is simple to examine at that point and least cost is incurred.

HENNIGAN: Thank you, Steve. Are there any questions on Steve Gaston's paper. Right over there, okay.

GRIFFIN: My name is Mr. Griffin, Mallory Battery, Canada. When you apply these to cells, how do you do the leakage testing?

GASTON: The leakage testing is both a helium-leak test and, of course, a chemical leak test. You apply -- actually the x-ray has nothing to do with the leakage test, completely independent test.

You can run your cover leakage test before or after the x-ray. Of course, it would be better after the x-ray, since it appears to me it's most desirable to have the x-ray done before it's welded to the cover and you cannot run a leakage test too well until it's welded to the cover and run a cover leak test.

GRIFFIN: I was wondering if there was any difference in water permeability, depending upon the amount of aluminum used in the seal.

GASTON: I don't think I understand your question. Could you repeat it?

GRIFFIN: Is actually that seal point an access point for water vapor from the cell or is it actually just a mechanical seal in the construction of the battery? In other words, is it possible water vapor could get out at that point and there would be a dependence on the composition of that seal, of the ceramic seal?

GASTON: No, I don't see how water vapor could get through that seal. Maybe Bob Steinhauer has an answer on that.

STEINHAUER: No.

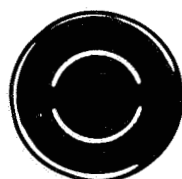
34**38****35****39****36****40**

FIGURE 6

GASTON: It's a completely hermetic seal. I don't see how water vapor could get through that.

STEINHAUER: It's a completely dense ceramic. There's no porosity to it.

GRIFFIN: Thank you.

HENNIGAN: Bob Steinhauer, did you have a question?

STEINHAUER: I'm curious whether you tensile tested the specimens and what were the results. I notice you didn't use back-up ceramic on the top of your seal. I'm wondering the rationale pro and con on that.

GASTON: The first question, did you tensile test, yes, we did. What were the values? I don't have them with me. I don't recall. I would have to get this to you.

Now, as far as the back-up seal, we do have -- we have two pieces of the ceramic, so I don't know what you mean by a back-up seal. There are three sizes. Maybe I should show you this slide again.

STEINHAUER: I didn't see the third one on that slide.

GASTON: I think the best one is Slide 4.

(Slide 4.)

Okay, I see. It's a little bit too dark to see. Maybe if I show you this slide, it will be better. It is there. I'll show you this slide. It's there. It just came out a little bit too dark.

HENNIGAN: We have one more question here for Mr. Gaston.

FEDUSKA: (Westinghouse) Are you permitted to describe the brazing alloy in the brazing technique employed in making the terminal 2?

GASTON: I don't think it would be for me to say. I think I could describe it, but I think the gentleman from Ceramaseal here, they can describe it if they so desire or have any comments on that. Are the gentlemen from Ceramaseal here?

BREDBENNER: (Ceramaseal) It's an active metal braze.

GASTON: I wonder if you could repeat that. The fellow over here couldn't hear you.

BREDBENNER: It's an active metal braze. The active metal is titanium powder and the braze alloy is silver/copper palladium.

FEDUSKA: It's done in the air?

GASTON: The brazing itself?

FEDUSKA: Is it done in the air?

GASTON: Is the brazing done in air is the question.

BREDBENNER: It's done in vacuum.

BOGNER: (JPL) Did you test any Ziegler-type seals?

GASTON: No, I didn't get a chance and mainly we didn't have sufficient funds to do that. I would have loved to do that. We just didn't have any funds in that program to do that.

HENNIGAN: Are there any more questions for Steve Gaston?

(No response.)

All right, we have one more discussion of seals this morning, which is a follow-on to Steve Gaston's talk, is Bill Harsch, from Eagle Picher.

HARSCH: Good morning. I'm Bill Harsch from Eagle Picher and I'd like to this morning talk about a ceramic seal improvement program that we've had going on in our plant. For the last year and a half we've had a company-funded R&D Program on ceramic to metal terminal seals. The purpose of the program was, or still is, to develop a non-corrosive long-life terminal for nickel/cadmium and nickel/hydrogen cells.

The program started with three manufacturers and a seal design compatible with each of the manufacturers was worked out. The design was based mainly on the manufacturer's processing equipment and also incorporating as many of the improvements in ceramic seals that had been made to date.

Each seal design was tested for electrolytic corrosion. It was tested as cells for cell performance, dynamic environments, and life cycling.

Today I will discuss the results of the electrolytic corrosion test. The test used was the Milliammeter Electrolytic Corrosion Test developed by Dr. Harvey Seiger at Heliotek. The test consists of charging a nickel electrode with respect to a counter electrode in potassium hydroxide. The test sample is electrically connected through a milliammeter to the nickel electrode as shown in the first slide.

(Slide 7.)

In this case, we used standard positive electrode from the nickel/cadmium and negative electrode was a nickel sponge and our test samples are connected as you can see in that slide.

The next slide, please.

(Slide 8.)

The test sample was electrically connected in this manner, in that one terminal was electrically connected in the circuit as was the cover blank itself. The reason we chose to do this was so that one terminal in the test -- I should say the brazed area of one terminal was electrically isolated from the test itself.

Now, we used our original design terminal, which has no stress relief collar. It's a 95 percent aluminum body with a silver copper braze and a Molly manganese metallizer. That we used as a control.

The second design tested was a butt seal geometry with a titanium hydride metallizer and a silver cup or palladium braze, which, of course, the butt seal has stress relief members. The second of the new seal designs was what's known as the "knife-edge" geometry with a niobal braze and a titanium hydride metallizer. This also had a Molly back-up ring, which we'll talk about in a minute.

And the last seal design was a butt seal geometry with nickel stress relief members and it had a zirconium base braze alloy and also a niobal braze to the cover.

Next slide.

(Slide 9.)

The results of the electrolytic corrosion -- this is the original design that we've used on many cells. As you can see, the little graph on the bottom, this seal had no potting material that is normally done on the top and bottom.

We got a corrosion current like this with a peak current of 75 milliamps. And then we had a weight loss of .102 grams after eight hours. And looking at the braze joints, this terminal is the one that was electrically connected with the cover. This one, brazed to the cover, was brazed to the ceramic on the terminal, was not in the electrical circuit.

As you can see, the corrosion of the brazed material on the braze to the cover, but no corrosion on this braze to the terminal. In this case, you have corrosion of both brazes. Next slide.

(Slide 10.)

We went -- the next one we put in -- you have one more. The next one was the same design but with the potting material that's normally put on the seal. As you can see, the corrosive current was reduced substantially. It had 11 milliamps. of corrosion current and the brazes themselves didn't show the corrosion.

Next one, please.

(Slide 11.)

That's eight hours. I might add the input to the test was 400 milliamps. and whatever you get from the other ammeter is due to the electrolytic corrosion. This is the other geometry which was the butt seal and the silver/copper palladium braze and titanium hydride system, and has a corrosive current of 11 milliamps. and it lost .06 grams.

And the last one, please?

(Slide 12.)

This is the knife-edge geometry seal, and it had a rather high corrosive current starting out and then it fell off to practically nothing. And coming back looking at the sample, as you can see, this has a Molly back-up ring, which the manufacturer put there to eliminate some differences in coefficients of expansion of the materials used. And this is basically corroded.

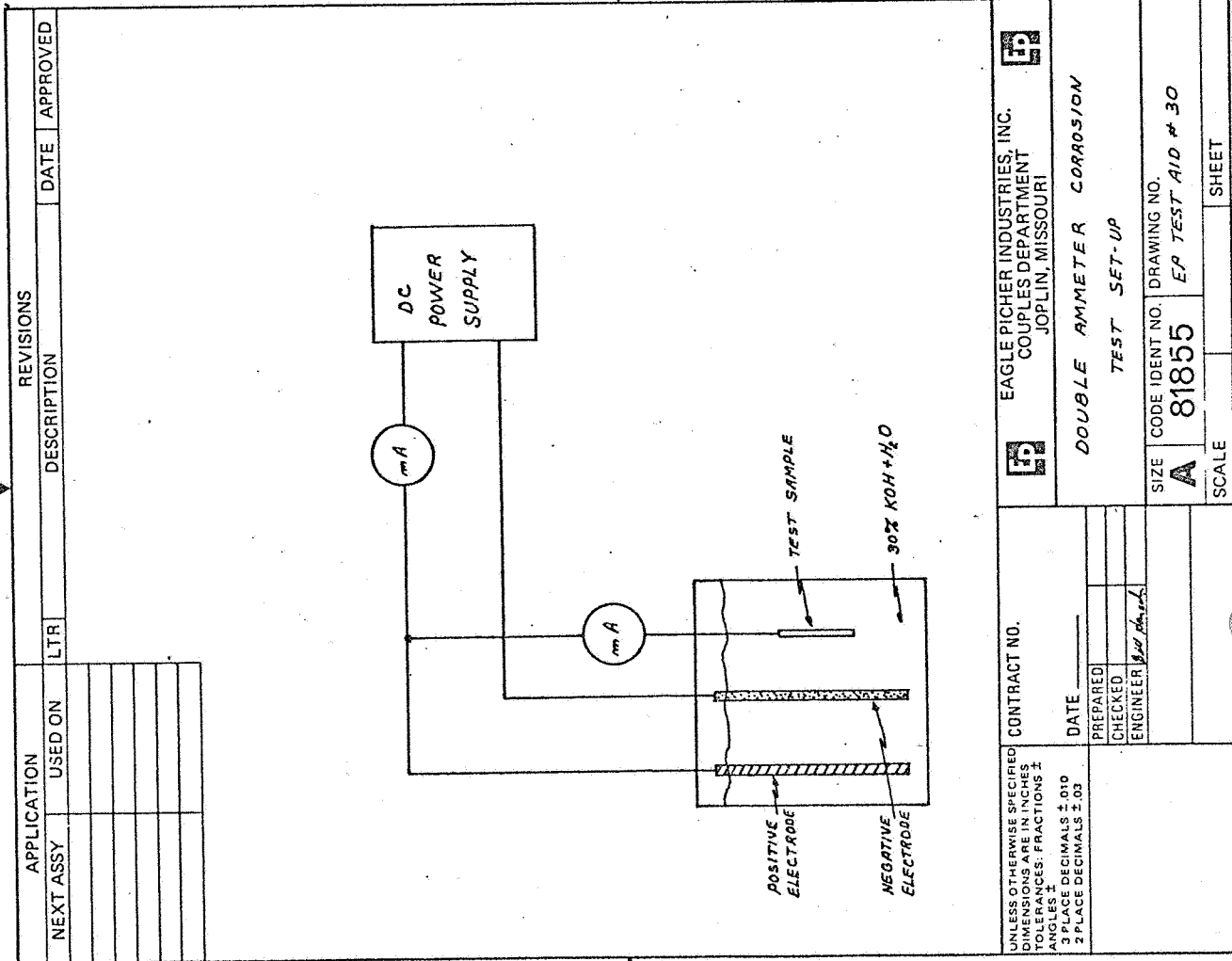


FIGURE 7

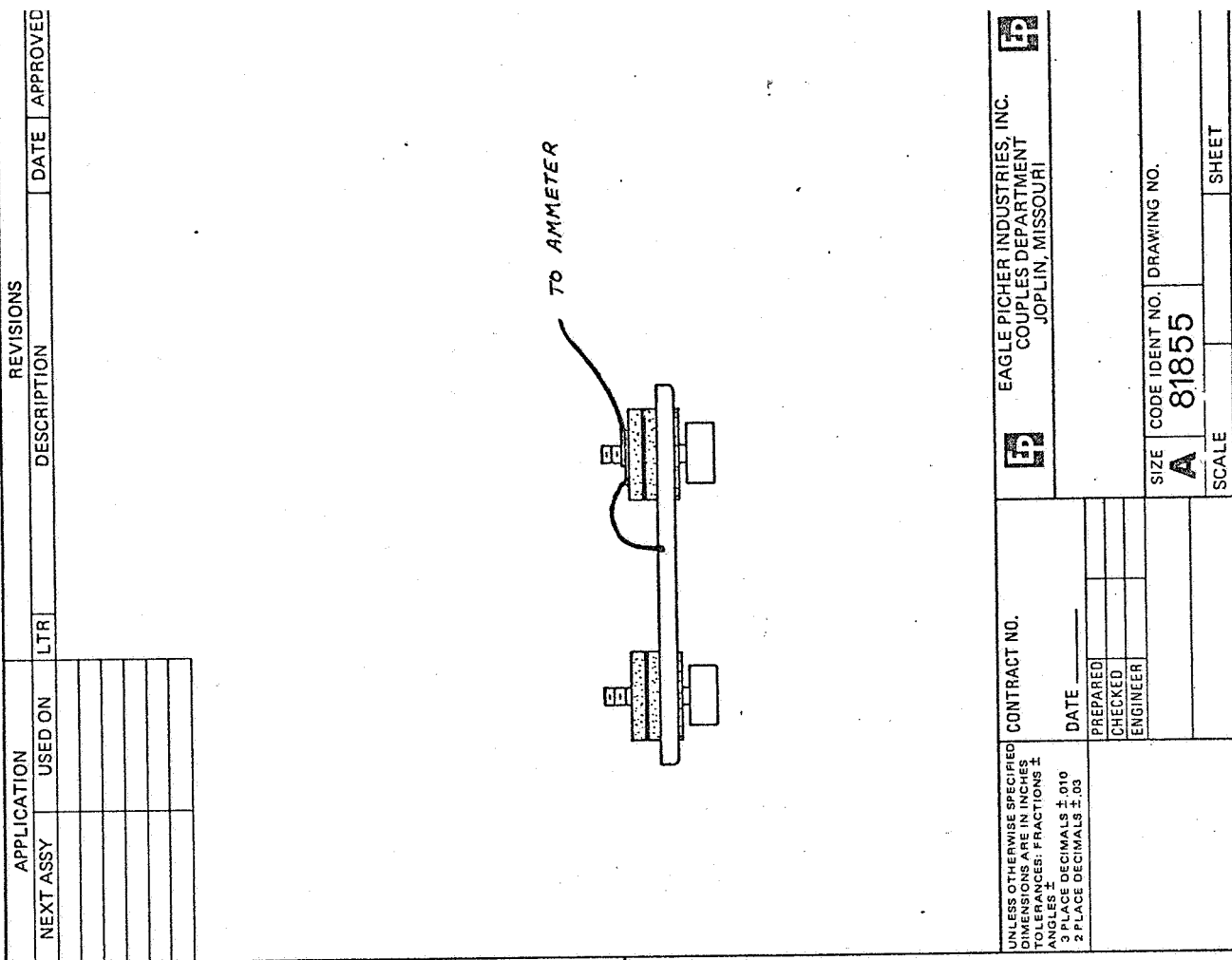
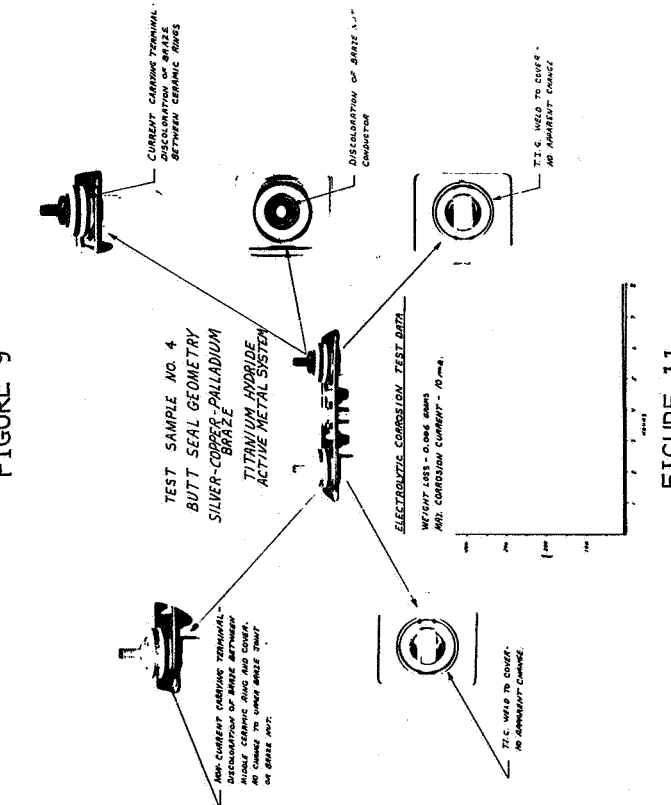
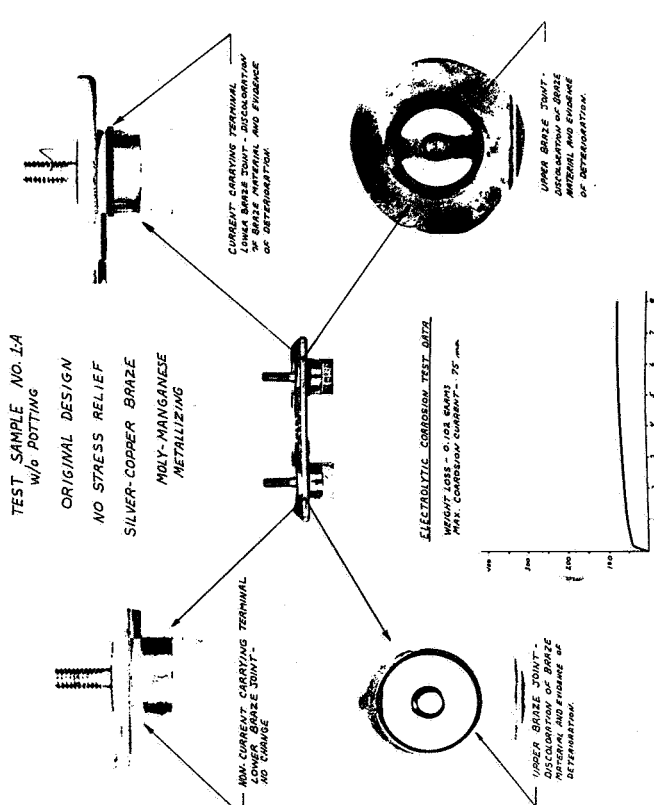
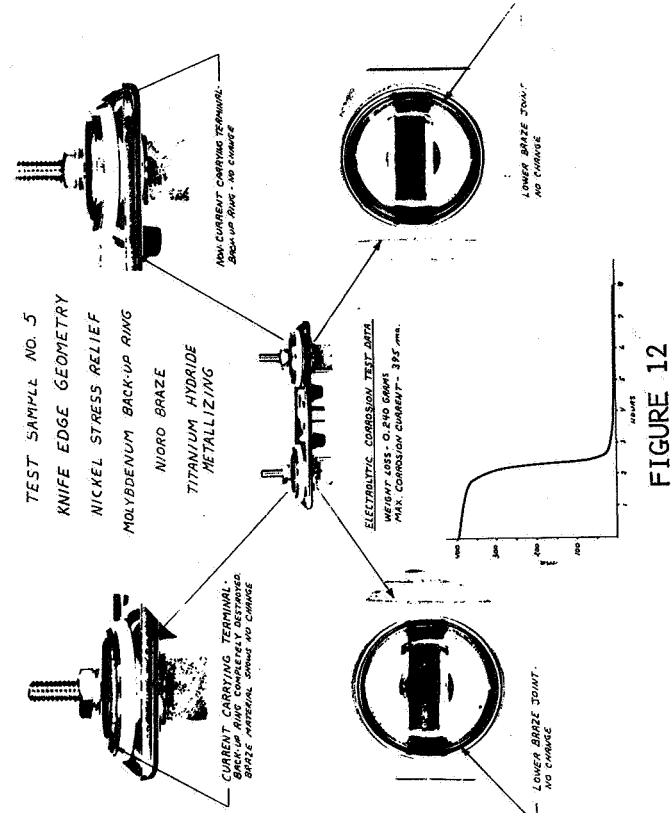
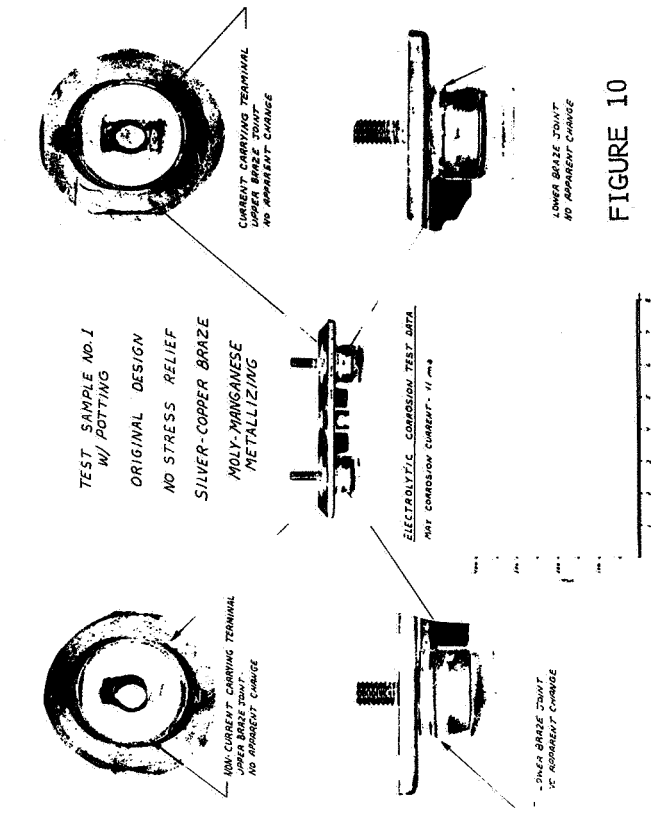


FIGURE 8



As you can see, this is the terminal that was in the circuit and the Molly ring is virtually gone from this design. But, however, there was no signs of corrosion on the nioral braze sections of the seal.

(Slide 13.)

And, finally, the last design, which is also butt seal geometry and a zirconium base braze. This design had no corrosion nor did it lose any weight. So, as of today, we're continuing the test. We have cells built with all of the seals that I've shown you on cycle life and it's a little early to tell anything.

There's only -- probably less than 1,000 cycles on any of these cells. Thank you.

HENNIGAN: Do we have any questions for Mr. Harsch?

Bob Steinhauer?

STEINHAUER: With regard to the last seal, using zirconium, did you find any problems with regard to the outline between the zirconium and the seal?

HARSCH: I don't know if I can answer that question. We don't have all of the data back on metallurgical parts of that terminal and I also don't know very much about the chemistry of it.

STEINHAUER: What percentage of aluminum was used in that last one?

HARSCH: I believe it was 99.5.

HENNIGAN: Dr. Font?

FONT: What is the voltage between your terminal during your test?

HARSCH: It was approximately 1.32-1.40 volts.

FONT: I asked you this because of the variety of the cells according to the variety of the plates. You are 0.5 volts above, between your positive cell and we are 0.8. I don't think that this kind of test represents exactly what is occurring in the cell.

HARSCH: You may be right. However, it is an effective means of looking for electrolytic corrosion. The numbers themselves are only represented numbers. I don't know if you can

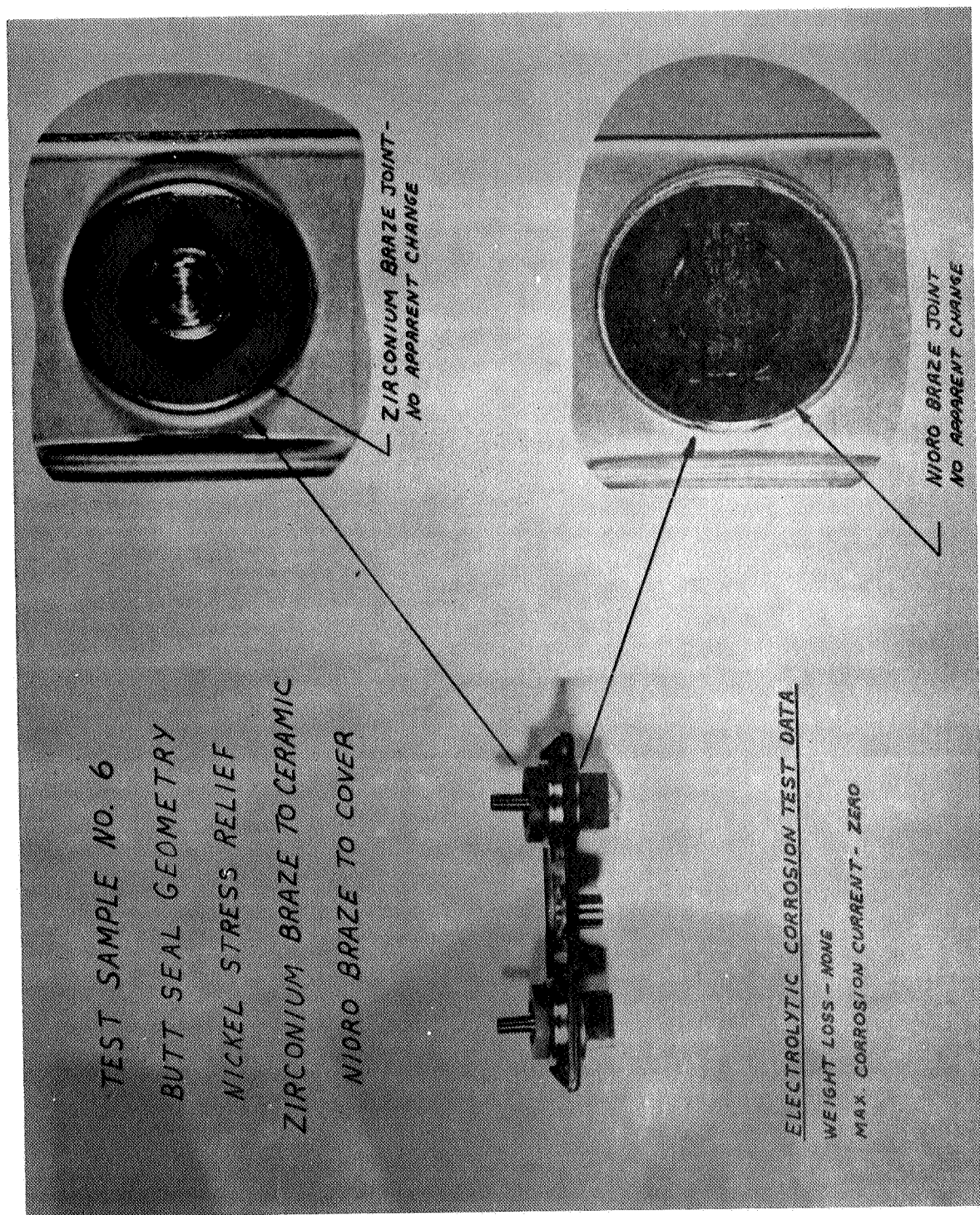


FIGURE 13

draw any firm conclusions to the currents or the voltages, per se. In fact, one of the very best methods of analyzing this data is by general appearance, by color and appearance of the brazes.

FONT: Yes, but I think you can't predict anything in this test. The second point is, when you are speaking about current, you have to measure also the area of the braze, which different designs of covers.

You have a very wide range of braze material which can affect the results of your intensity.

HARSCH: I agree 100 percent. However, what we were looking for is no corrosion, rather than some degree of corrosion.

HENNIGAN: Bob Steinhauer?

STEINHAUER: I would like to comment on a question Dr. Font asked. The purpose for the higher voltage is generally to create an over-test condition on a short-term basis for rapid evaluation of seal materials.

It is true it is not a light test, but it is a screen for materials.

LURIE: I'm Charles Lurie from Gulton. Imposing too high a voltage can do something other than accelerate the test. There is a threshold value below which corrosion will not occur and was any attempt made by voltametric means to be sure that this threshold value was not exceeded or that you were at a realistic voltage?

HARSCH: No. Again, like I said before --

LURIE: Is it possible that using a double ammeter test and not using a voltametric means to back it up, that you exceeded the potential that could occur in the cell and that you were seeking a corrosion mechanism that wouldn't occur in a nickel/cadmium cell during normal operation?

HARSCH: I don't know that for sure. We didn't perform that part of the test. We were looking for corrosion.

LURIE: Of course, it is possible to make virtually any system corrode if you increase the voltage?

HARSCH: However, the testing done by Steinhauer and his people on materials pretty much dictated what materials we were using with the one exception of the zirconium based braze alloy. And so we had a pretty good idea of what the corrosion potential was of the materials in the seal.

HENNIGAN: I believe that's Harvey Seiger that would like to ask a question.

(Laughter.)

SEIGER: I would like to make a comment, if I may. The test was developed in order to determine whether there are problems. It's not only a corrosion test, but one can have a lower over-voltage and therefore affect the charging of the positive electrode or the affect of charge-efficiency of the positive electrode.

And, as you say, you weigh it, you look at the colors, and that will tell you whether you have corrosion and you can look for bubbling, and that will tell you whether you have a lower oxygen evolution potential.

The positive electrode is in there to maintain -- one could do it voltametrically or this easy, inexpensive way. If you had a positive electrode, you can simulate conditions inside a cell. So you charge this positive electrode, you pass current through it, and you can bring the potential up to a realistic potential, you can discharge it, bring the potentials down to a realistic potential, and see what the kind of distributions there are.

Now, the ideal thing, as Dr. Font recognizes, is to have a sample of the seals that one's using. If one does that, they can have an idea of the fraction of the current that's going to charge a particular electrode and this seal that you're investigating.

HARSCH: Thank you.

HENNIGAN: We have one question from Aiji Uchiyama.

UCHIYAMA: Have you run any tests of a thermal cycling nature? In other words, planning a test along that line?

HARSCH: Not in our present program. We're going to continue the life testing. At some future date, I'm sure, we'll be doing thermal cycling in order to fully qualify the cell.

UCHIYAMA: How about Steve Gaston?

HARSCH: Steve, do you have any comment on thermal cycling?

GASTON: What was the question? I wasn't listening -- cycling of the terminal?

HARSCH: Do you plan to or have you done any thermal cycling on this seal?

GASTON: No, I have not and I don't plan to. I have no more funds.

HENNIGAN: Did you have another comment, Bob? Bob Steinhauer?

STEINHAUER: Yes. I think that the voltage used in your test is not unrealistic if you are using a single terminal header. Secondly, with regard to thermal cycling, I think most of thermal cycling is achieved brazes cycle itself. It's not cycling compared to what the cell sees in orbit.

I guess I would like to ask the question that I asked Steve. Did you perform on any of these seals tensile testing?

HARSCH: Yes.

STEINHAUER: What were the end results?

HARSCH: In all three designs that were tested had adequate strength when tested tensile, in the order of 500 to 600 pounds, if I remember right.

STEINHAUER: Do you happen to remember what area, what braze area this was in?

HARSCH: No, I don't.

STEINHAUER: One last comment. I would think that the choice of zirconium is a good one.

HARSCH: Norm Anderson had a question from ILC.

ANDERSON: Yes, I'm the one that made the zirconium braze plugs for one of these tests. I could probably answer a couple of the questions that came up.

With regard to thermal cycling, we used the same braze for a variety of arc lamps that we make and routinely recycle these brazes. They are quite resistant to the thermal cycling conditions.

We have measured the tensile strengths using seal M-15 and the dumbbell specimens, measured strengths along the order of 7,000 p.s.i.

The ceramic test was used on the seals that Bill tested. I think the strength could run quite a bit higher with a stronger ceramic body.

STEINHAUER: Did you put air on it?

ANDERSON: I don't think there's any problem -- the ceramic metal base is a simple way of attaching the metal to different locations.

STEINHAUER: You say brazing to ceramics is strictly zirconium.

ANDERSON: I'm not saying that.

HENNIGAN: Are there any further comments or questions on ceramic seals or Ziegler seals?

If not, we will proceed on to the separator discussions this morning. Our first speaker in that area is Dr. Will Scott, of TRW Systems, who has some information on polypropylene types of separators.

SCOTT: I might have one comment on seals before I talk about separators. We have had in-house approximately 50 amp. hour cells with large size terminals made by the Microwave Tube Division of General Electric with a butt seal design, all nickel parts and essentially nickel brazed, no silver, copper or molybdenum.

These cells have been in-house on test and storage various configurations for about eighteen months at this time and we have seen no trace of any form of contamination, corrosion, leakage, discoloration or any defects whatsoever in any of those seals to date.

As far as I am aware, that particular size and configuration of seal that we put in those cells had not been made before by G.E.

And they did a good job, apparently.

On separators, I'd like to describe some results that we have seen in some comparative tests on 20 ampere hour cells manufactured by General Electric, containing three different kinds of separators: pellon/nylon 2505; the original polypropylene, designated FT-2140, which was supplied originally by Pellon; and another polypropylene GAF, WEX-1242.

The first viewgraph shows the essentials of a test program.

(Slide 13a.)

We had a total of 12 cells in four groups of three with the letters designations M, N, R and S shown there. There were three cells each with the two polypropylenes and then there were six cells with nylon tested in the electrical circuits, three at a time, a total of six cells with the nylon.

The test parameters are shown at the bottom there, operated with a base plate controlled at five degrees led at Centigrade. Two different lengths of cycles were used at various times during the test.

The depth of discharge was changed a couple of times for various reasons, from 15 to 18 ampere hours, which is a fairly high depth of discharge. The recharge was either two amps or two-and-a-half amps, depending on whether it was an eight or a twelve-hour cycle time that was used.

The recharge ratio was kept close to 1.25 amp/hour recharge ratio. This test was intended to be relative to a synchronous orbit application, but it is an accelerated type of test in that there were lots of cycles conducted fairly close together. The cycle sets were interrupted at certain intervals with various periods of trickle charge.

And this will be indicated on the subsequent slides. And next slide, please?

(Slide 14.)

This is a summary of the chronology of the test. This test is now completed. At the end of the test the groups M and N had been on test for a total of 866 days and the R and S, which were the nylon types, were 738 days. And you can see on down the list there the total number of cycles and days and so forth on this test up until the time that it was terminated.

Next slide.

(Slide 15.)

This is a group of end of discharge voltage. At the end of each of various representative cycle sets, that is, where, say, 20 or 30 or 40 cycles were conducted continuously. This is the voltage at the end of the last discharge of that set as the number of cycles accumulated.

As indicated there, the depth of discharge was changed a couple of times. It indicates that, as you see, that there was really little change in the end of discharge voltage until all the cells had exceeded 500 cycles under these conditions and, in most cases, until they had all exceeded 600 cycles.

Then, after 600 cycles the one cell in group N went down rapidly in voltage and ultimately failed soon after that.

In group N there's a 2 after the N, which means there is only two cells left in that set. And then after the next 165 days of trickle charge, a second cell in group N had failed and so that group of cells was taken off the test.

And one cell out of group M, at that time, is shown below .95 volts, which is really not too bad of voltage for this depth of discharge. In summary, under these test conditions, we did get over 600 cycles at from 15 to 18 amp/hour discharge for every discharge out of these 20 ampere hour cells, which I consider to be a pretty fair performance.

And you can see that up until 600 or so cycles the polypropylene separator cells held their own pretty well with the nylon cells. But after that, for reason which I'll mention in a minute, several of the polypropylene separator cells failed.

(Slide 15a.)

I believe the next slide will show some data on internal impedance is measured at 60 Hertz for these cells. Initially, their impedance was all quite similar, and in the range from $1\frac{1}{2}$ to $2\frac{1}{2}$ milliohms.

At the end of the testing the various impedences were as indicated in the next column.

You can see that of the two groups of polypropylene

cells, M and N, the impedances of cells in group M had increased slightly. One cell in group N, which was the GAF separator material, had increased hardly at all, whereas cells 2 and 3 in group N, had increased drastically.

All three cells in group N were torn down at that time. The cells in group M were kept standing by and approximately three months later, one of those cells was torn down and the impedance was measured again at the end of that three-month period and you can see that in cell 2 of group M the impedance had increased to 18 milliohms.

When the cells were torn apart, it was found that the separators in cells 2 and 3 of group N were very dry. In fact, there was no indication of any wetness or any electrolyte in those separators.

The KOH content was determined by titration and found to be approximately 5 to 10 percent of what was calculated to have been in the separator when those cells were new. One cell in group R, cell number one, has also been torn down, at least so far, and the KOH in the separators in this cell, which were nylon, was determined.

The KOH content of those separators was approximately 75 percent of what was calculated for a new cell.

The next slide shows some photographs of separators removed from various cells. Although these don't tell you too much, it gives you a feel for the typical appearance of the separators as removed from these cells.

(Slide 16.)

This is from group N, cell 1, which was the low-impedance cell of the three that had the WEX-1242 separator in it and was still reasonably wet in this cell. The next photograph is a typical separator out of cell 2 of group N, which was the worst cell in terms of high resistance in separator dryness.

(Slide 17.)

And it has a noticeably more dark-gray material on the separator. The side of the separator that you are seeing here is that side facing the negative plates.

There was no visible discoloration or deposits on the opposite side of any of these separators, that is, the side facing the positive plates.

Then, the next slide shows the typical separator out of the third cell in group N, which was also a dry, high-impedance cell at the end of the test.

(Slide 18 not available in this transcript.)

And you'll notice that it has less, actually less visible deposit than the cell that was wet. I merely point this out because there is some evidence in certain kinds of cells that the amount of cadmium migration seems to be higher in cells that get dryer and less in cells that operate wet.

I did not see this type of correlation whatsoever in these cells. The last slide, shows a typical separator out of the cell from this test that we've taken apart to date that has nylon separators.

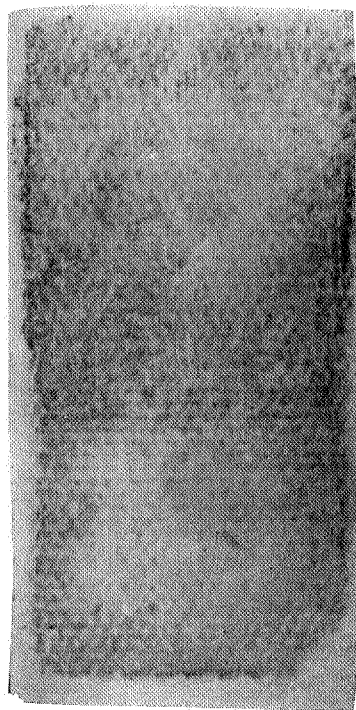
(Slide 19.)

In every separator in this cell, the top upper two corners of the separator were dry and all of the electrolyte was concentrated in the shape that you see darkly colored here.

I can only speculate that when the electrolyte was added to this cell, it went down in that pattern, spread out, and never did get up into the upper two corners.

Note also that the amount of discoloration in general is approximately the same level as observed in many other cells containing polypropylene, wet or dry.

One conclusion that one might make is that there appears to be a certain number of days, number of cycles or combination thereof for which polypropylene separators appear to be comparable to nylon in terms of cell performance at low temperatures.



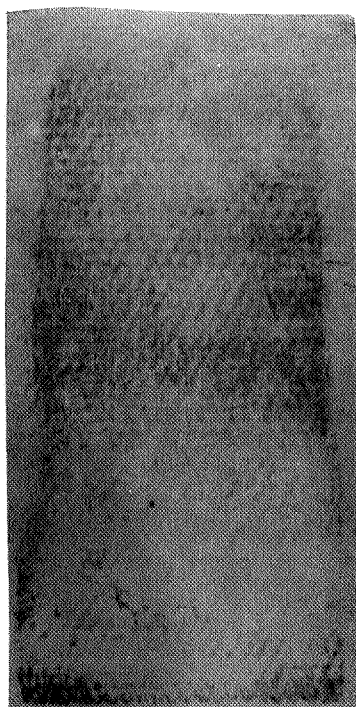
Photograph of a Typical Polypropylene Separator Bag from a Normal (Wet) Cell

FIGURE 17



Photograph of a Typical Nylon Separator bag from a Normal Cell

FIGURE 19



Photograph of a Typical Polypropylene Separator Bag from a High-Impedance (Dry) Cell

FIGURE 16

FIGURE NOT AVAILABLE

Beyond that, there appears to be a loss of electrolyte from the separator which produces a dry separator condition, therefore a high impedance in the separator, and therefore a high voltage charge and a low voltage discharge condition.

It's not clear to me just what combination of cycles, depth of discharge, temperatures and time are good and bad for polypropylene separators versus nylon right now. I think this still remains to be demonstrated by further testing. That concludes what I have to say.

HENNIGAN: Thank you, Will. We have a couple questions here. Jim Dunlop, from Comsat?

DUNLOP: I have three questions. How did you remove the separator? Did you have any trouble removing the separator?

SCOTT: None at all. It was -- well, I'd say there was only the slightest amount of sticking, but in most cases the separator slipped right off with no force at all.

DUNLOP: Independently of whether it was polypropylene or not?

SCOTT: No, I would say there was more sticking with nylon than with polypropylene. It was sort of independent, in this case, of the degree of wetness, at least in these cells.

DUNLOP: The other question: we observed similar results with the testing we did with nickel/hydrogen, where we were testing different types of polypropylene. One would be, we called Achilles, the other being Hercules.

We did find the same thing. We tried out the separator. The other thing that we did observe, and you probably observed the very same thing when you took the separator out it would no longer absorb water.

SCOTT: Yes, I saw the same thing. These separators had different wetting characteristics entirely than they did when they were new.

DUNLOP: Did you draw any conclusions on this -- as to why?

SCOTT: Well, only a theory and that is that, first of all, the wettability that you observe on these polypropylene materials that we used when they are new is strictly a function of the surface treatment that is applied during manufacture.

We did not wash out these materials. They were as received materials. I think it is becoming fairly well known that this wettability is washed out in the body of the cell during cycling in one way or another.

So, I can only conclude that the wetting agent, or whatever you want to call it, has dissipated. It probably ends up somewhere in the cell, probably in the plates.

DUNLOP: Were these bag separators?

SCOTT: Yes.

HENNIGAN: Steve Gaston?

GASTON: I just have a comment on our experience of using the polypropylene separators on the other amp hour cells. Even though I don't have any long life test, we found initially that polypropylene separators have a lower capacity if you wash out the wetting agents.

It's generally about 10 or 15 percent lower than the nylon cells. That's the only problem I have right now. If you wash the wetting agent out, you will get lower capacity.

HENNIGAN: Thank you, Steve. Harvey Seiger?

SEIGER: Is anything done to avoid an electrolyte redistribution when these cells were originally made?

SCOTT: Not in these cells.

SEIGER: Thank you.

SCOTT: One more comment -- you know, you can make nylon do the same thing. You can, if you do the same thing to nylon as you do with polypropylene, even initially, it is, you can make it very non-wettable, so there, you know, isn't that much difference in certain characteristics between nylon and polypropylene but there is a difference in the terms of the performance, long-term performance of nylon versus polypropylene in these cells, for reasons which have been, I think, theorized on here before.

SEIGER: Since you commented, may I make another question? When you took these cells apart at the end after they've gone through all their cycling, did you then notice any difference in wettability between the nylon and polypropylene?

SCOTT: Very little.

SEIGER: Were they both dry?

SCOTT: Well --

SEIGER: Both of them not able to wet?

SCOTT: Yes, we like to look at this under a microscope and you can put the separator down, you can drop a drop of electrolyte on there and you can sit and watch it all day and it just sits there on either one. Whereas, when they're new, it'll, well, actually it's interesting.

On new nylon, it takes about five minutes for a drop to disperse. On certain of these new polypropylenes -- it's "zap" -- it's gone in about three seconds. So, it just looks like it's almost the reverse when they're new.

Dr. Font?

FONT: I have a question. Have you measured the weight loss of the separator before manufacturing?

The second part I have: do you have the same amount of electrolyte in your cells with nylon and with polypropylene?

SCOTT: These -- I might say that this test was a, was not a highly-controlled test. It was a test of commercially available state of the art cells as of about two years ago. So, we had no opportunity to measure the weights of the separators, initially, so we don't know what the weight loss is.

And the amount of the electrolyte was that which was recommended by the manufacturer at the time the cells were built and it was different between the two different cells.

HENNIGAN: We had a question over -- back there.

GRIFFIN: One thing -- each year we talk here, going back from 1970, 1971, 1972, the same comments come up. The one that immediately comes to mind is, "How is the cell filled?" Was it air-removed from the separated composite from the

electrodes and then the electrolyte put in. I think this was mentioned last year.

One fundamental thing about getting the air out of the separator, getting out air of the system before you can put the extra (block) in. Then this rises the question of peculiarity because we're all talking about wet-out.

But, yet, really I would think that a wetting agent really doesn't make that much difference to the total wetting space available. In other words, how much electrolyte you can get into the spectrum.

With the nylon and polypropylene, we've got a pretty hydroscopic structure anyway. We wouldn't expect the wet-out to be all that great and the only reason that the polypropylene works is because of that extruding agent on the other side.

And nylon is pretty slow anyway, so the vacuum system is very good. And in both cases I'd also like to point out that one thing that is very, very important when we're dealing with very smaller cells, and I think this might be constituted in your business too, is the control on the initial product that the separator manufacturer sells us.

I know Eagle Picher has a very full specification for nylon. I've yet to see one for polypropylene put into your reports and I think there is a fundamental difference that if you're after something for the last ten years and you put such a heck of money into that and such a lot of effort into evaluating all of this work, you should at least put the same proportion of money into the starting point.

I would like to see you even consider taking each separator and deciding: (1) do we use the same thickness in each case or do we actually start off with the same compression pressure of electrodes on the material?

I'd like to see these questions answered to really help this final analysis, which is, you know, very detailed and very, in one sense not controlled, because each time we come to the question, "Was it drawing out of the GAF or the polypropylene or was there something wrong initially when you put the cell together?"

And the final comment: someone said last year, "When you're designing accelerator tests," he suggested that you should be really certain in the ideal case, that the failure mechanism at the end was the same as the failure mechanism, in say, ten years.

I would like to ask one final question, after that speech. Was the failure mechanism, in your opinion, are these cells similar to what one would expect on a five-year life cell or how many orbits of space orbits one would consider for this type?

SCOTT: Shall I answer that?

HENNIGAN: He was making comments primarily.

SCOTT: As far as I know, there is no established history of life-testing, real-time life-testing of polypropylene separators, that is, in the sense that there are known failures that have been analyzed in the mechanism actually established for real-time life tests in excess of a couple of years or more.

That may not be strictly correct, but it's not well-known at least, so I don't know that we have anything really to compare it with, at least especially for a five to seven year mission.

HENNIGAN: I was just going to say that tomorrow we'll have a talk by Don Mains on the Accelerated Test. That's actually a planned test to correlate long life with very short stress cycling.

And this is a very, at this time it's a very big test you have to run to get an accelerated test that we hope will come down to an economical test. So, tomorrow, he'll be discussing that just for your information.

Lou Belove?

BELOVE: Dr. Scott mentioned real-life time. Now, I think the Canadian is here, but we have some data on real-life time of polypropylene cells.

SCOTT: You don't have established failures that have been analyzed, though. That's my point.

BELOVE: I think we have more than ten years. I would like to bring this up: we do know that polypropylene cells have been in orbit for more than ten years and they are functioning successfully during that period.

SCOTT: That's right, at ten percent depth of discharge.

BELOVE: Right, so that we have to know this, that whether it's a depth of discharge or whether it is actually the types of polypropylene or -- there's one thing I didn't

hear -- how much KOH was added to these cells? What was the difference between the nylon and the polypropylene in the cells in the amount of KOH added to them?

SCOTT: Yes, do you mean percentage-wise?

BELOVE: Because the tendency is -- or has been, I should say -- has been in the past used far less KOH than polypropylene.

SCOTT: That's right and in this case that was the direction of the difference.

BELOVE: Might it not be that situation that created this drying-out effect?

SCOTT: It certainly might. I think it's becoming clear that could be a major cause of this problem, but, you know as I say, that wasn't that clear two years when this test was started.

HENNIGAN: I think it's an unfortunate -- the fact when I talked later on the -- we have (salisman) and cycle for, you know, three or four years, and we're taking looks at separators now. And way back then, you wish you knew what you knew now.

Floyd Ford?

FORD: (NASA-Goddard) In regards to Lou Belove's comment, I think it should be pointed out that those are cylindrical cells that he is referring to. And along that line, I had a question for Dr. Scott.

I think we're failing to look at the cell as a full-integrated system. When you look at a cell and analyze the separator, you look at it as a complete component of the cell. But the cell is a very dynamic environment and the point is simply this: I can't accept the fact that mechanical pressure that is created first when a cell is assembled, second, with expansion and growth of positive plates with cycled life, as has been documented that this is not a significant factor, and this rediffusion of the electrolyte.

So, the question is, did you look at the positive plates or did you try to locate where the electrolyte was? If it wasn't in the separator, do you know where it was?

SCOTT: I'm not sure where it all is yet. We have analyzed the plates for potassium hydroxide. I can account for

something like 90 percent of the original KOH that was added to the cell. I know that there are some tricky things about trying to find all of the KOH that you put into a cell after a long cycle life.

I'm not sure that I know exactly how to do that. But with a fairly simple approach of pulverizing and analyzing the plate materials, I can show where most of, where there has been a migration of potassium hydroxide from the separators into the plates.

FORD: Which plates in particular?

SCOTT: The negatives, primarily.

FORD: In the negatives?

HENNIGAN: Bob Steinhauer?

STEINHAUER: Do you believe that your impedance measurements and perhaps the observations made on separator dryness depend upon the state of charge of those cells, when opened or when measured? And in particular, when opened for the cells strapped out with resistors.

Should we be looking at this sort of thing before evaluating the electrolyte?

SCOTT: When a cell is in fairly new condition with respect to electrolyte distribution and because of that the impedance is pretty low and fairly, let's say, normal, which you'd expect.

I believe it is important to know what the state of charge is and what the -- and a number of other factors will affect the exact value of impedance that you measure.

However, when the cells are in the condition that certain of these I mention here are, with respect to dryness of the separator, it doesn't matter what you do to that cell, you always get a very high number.

We get essentially the same number whether it's charged, discharged, or anything else. In other words, that high resistance is dominating, in the separator, is dominating the results that you get.

And you can't change that no matter what you do. Excuse me, one more comment. I do know that, for example, in fairly new cells that are marginal as far as electrolyte is

concerned, if you discharge them very deeply, you can get a relatively high impedance versus the value you measure when they are fully charged because you are using up water in the discharge process.

And if they don't have enough electrolyte you can tell by measuring the impedance when they're completely discharged. That's a nifty little thing to do, if you're concerned about electrolyte.

STEINHAUER: Well, when you open these cells and we keep talking about sticking in a sort of a relative term. If you open the cells after they've been strapped out versus opening them at, say, 50 percent state of charge, then you would make a different observation?

SCOTT: I think you would at a certain stage in the migration of the electrolyte, maybe some intermediate stage. I still feel that when cells have gone as far as these two high-impedance ones are, that it wouldn't make any difference.

HENNIGAN: Rowland Griffin?

GRIFFIN: One interesting thing that came out a while ago was that Hercules was the only material that I remember anyone ever seeing that absorbed more electrolyte initially than pellow.

And, it was used in some cells described last year and the year before and it came up rather well, I think Dr. Hennigan's electrolyte test.

One thing, in looking at the three materials you put on the board, the pellow 205 has certain -- well, let's say 1.5 for argument's sake. And the FT 2140 was a material design in Germany that was similar, 1.5 approximately.

So we have two different, with similar (denier). So we have a high electrolyte absorption here. The WEX 1242 is probably similar, about three (denier). You expect a lot much difference due to the fiber construction.

One has to come back to the final answer, "Well, what is happening to the electrodes as a function of time?" If you take similarity polarity forces and consider this: if the two were the same, one would expect the electrolyte to stay there and cycle backwards and forwards depending upon what you're doing to the charge cycle.

But if, for instance, you are actually getting an aging process in one electrode which leads to a much finer

force on it, one would expect the polypropylene and the nylon to have a similar result. I would like really to try to establish on these results, did you feel the nylon was losing or do we not have enough data on this point?

Did the nylon lose the electrolyte the same as the polypropylene or do you not have anything to confirm it? Because the impedance measurements did not show any of the nylon cells to be damaged.

SCOTT: I think I mentioned that chemical analysis of the separators removed from the one nylon cell that we've torn down in this group showed about 75 percent of the KOH content that we calculated for the new condition of the cell.

Now, it is uncertain as to what the so-called new condition content of the separator is. This is a number which is, I guess, like plus or minus 25 percent in terms of our ability to estimate that value.

So these are rough numbers. We did not, have not made this determination directly on a brand new cell. It's something we'd like to do.

GRIFFIN: One final thing -- we do get these in primary cells, you're not alone. Polypropylene, especially when you store it at high temperatures, 160 degrees and up, you can get the same sort of dryness in a polypropylene system.

We can't show that for nylon because we can't get nylon to stay in that temperature for the length of time involved and one tries to go to polypropylene.

But the real question is: "What happens to the electrolyte?"

HENNIGAN: Well, last year we got -- the data I showed on the nylons, Hercules and other polypropylenes, we did have 26 cc. in the nylon cells, which is are 6 amp/hour cells and 24 in the polypropylene cells, like the GAF material.

In that particular polypropylene cell, there is an electrolyte in the bottom of the cell when you open them. And nylon retains it and keeps it worked up where you just can't get enough into those polypropylene cells to keep them wet.

HENNIGAN: Mr. Dangel?

DANGEL: Generally, considering the factors which make the fabrics absorb, there are three considerations, primary considerations. The first one is the nature of the fiber, the second one is the surface materials on the fiber and the third one is the structure, the geometry structure of the fabric.

I think it is fairly obvious that the polypropylene fiber stays and doesn't probably change very much here. I think it's equally obvious that something happens to the surface after they disappear or disintegrate or something else happens to them. This has a major effect on the re-wetting.

But the thing that I'm wondering about -- and I wonder if you have observed this -- is what changes happened to the geometry of the fabric. Does this charge or discharge, separate the fibers from each other?

Does it make it bigger on the microscopic scale? Did you have a chance to observe this?

SCOTT: I wasn't looking for that type of thing, but I have looked at those separators under, I'd say, 20 power and I have looked at new ones under 20 power and, offhand, I did not see any difference that I could notice under those conditions.

HENNIGAN: Sam Bogner?

BOGNER: I would like to make one other comment to the piece of the puzzle -- that is, the fact that if you sterilize these materials, you get different results. I wonder if people have considered that.

HENNIGAN: This is polypropylene?

BOGNER: Cell capacity goes up and internal resistance goes down.

HENNIGAN: This is for polypropylene separators, right?

BOGNER: It also occurs in membranes and silver/zinc cells.

HENNIGAN: Floyd?

BOGNER: The temperature is around 135 C. for 100 and some hours.

HENNIGAN: Floyd Ford?

FORD: Yes. Dr. Scott, if I understood what you said, during your presentation, it was that the drier the separator the more apparent cadmium was in that separator?

SCOTT: Not in these tests. There was no apparent correlation between dryness and the amount of deposit on the negative side of the separators.

What I did say was there was some discussions in the last couple of years at this meeting which suggested that as cells dry out the cadmium migration tends to increase, or at least there seemed to be some indications in that direction and I just said that that did not seem to be the case here.

FORD: I think it's fair to say that's not an unnecessary condition.

HENNIGAN: Barry Trout?

TROUT: On these cells, I assume they were hermetically sealed cells and if they were, did you have pressure measurements on the cells and did you notice any significant differences between the separators?

SCOTT: Yes, they were indeed sealed. We indeed made pressure measurements. In fact, most of the time we had transducers on them and we have permanent records, continuous records of pressure during the whole test.

I have not really sat down and tried to analyze all of that data, but offhand, I would say that there was little difference in pressure behavior. Let's say during the normal conditions -- when the conditions of the cells were normal, say, with respect to this impedance and probably drying problem -- interestingly enough what happened in those cells that began to dry out was the pressure began to drop.

And I think that this is what you would expect if you, you know, as the cell begins to dry out. You actually decrease your recombination pressures.

HENNIGAN: Jim Dunlop of Comsat?

DUNLOP: I'd like to make a general comment. Our testing with different separators in the nickel/hydrogen cell is a little different from nickel/cadmium. You don't get any cadmium vibrations, so you do eliminate that particular problem in the cell.

The separator always comes out relatively clean. We have tried a variety of Hercules and Pellon polypropylene separators. It is true, just like you said Dr. Scott, you get a deeper depth of discharge.

It's a way to observe a value quicker. When we go to very deep depths like 80 percent of capacity, you can very generally quickly fail in all of the polypropylene substances we use today. The very best we can get (inaudible).

This argument seems to be centered between nylon and polypropylene. Frankly, there may be other better choices than these two to obtain long-term results.

HENNIGAN: I would just like to make one comment. When I found out unfortunately last year -- it also depends on whose cell you put what separator in because that Hercules separator when we tried it in another manufacturer's cell of General Electric, it just wouldn't work under the same performance we got in the Eagle Picher cell.

So, it's pretty hard to cross over results between manufacturers.

Mr. Griffin?

GRIFFIN: Potassium titanium is interesting because in that we're the people who used it. Well, Dupont withdrew it's -- I don't know whether people are getting the same results with different structures that they had originally.

It is really a question of who has tried this.

HENNIGAN: Marty Klein?

KLEIN: We've never used the (lead) products. We were always working with basic Dupont products, so there has been no change in our starting material. I think Jim's comment is valuable.

Our thinking, and I'll talk more about it tomorrow, but basically we look for material that would wet naturally by it's own contact angle with the electrolyte. Potassium hydroxide as opposed to using these nylons or polypropylenes which really depend upon the wetting characteristics by a third agent, it has worked out very well.

We have an enormous amount of data showing the material is quite stable, will hold electrolytes. And I think it's a pretty good material to be looked at for nickel/cadmium.

There are some different criteria for nickel/cadmium than for nickel/hydrogen, but certainly looking at inorganic materials that wet directly is a valid approach to look at.

HENNIGAN: A comment from Guy Rampel from General Electric.

RAMPEL: I'd like to comment on your last line, Dr. Scott. I feel it showed relatively clean separators at the top. I feel that that is getting unavailable cadmium in those areas due to high current density.

DUNLOP: Where does the cadmium go?

RAMPEL: It's still there, but it's inactive at the electrode chemically by taking in the depth of discharge exercises.

SCOTT: Guy, though I think I know what I heard you say, but those top corners of all of the separators were dry as a bone. Now, maybe that's something that's normal to you, but the gray area was very wet, the top corners were dry.

So, which is the cause and which is the effect?

RAMPEL: That's just what I was going to say -- what came first, you know, what started first to give you that result at the end.

HENNIGAN: If we don't have any more comments or questions, we ought to take a coffee break now. Thank you very much, Dr. Scott.

(Whereupon, a short recess was taken.)

HENNIGAN: I'd like to remind you again to sign the attendance sheets, unless they're both still circulating. We'll continue on with the separator area for the remainder of the morning, which will go until about 12:45, when we'll take a break for lunch.

I'd like to remind everybody to please buy their cocktail tickets before morning. We'll have to close it down at noon, at 12:00 or 12:30, whatever.

I'd like to discuss some of our work in the separator area for the next few minutes. And the first slide will be kind of a reminder of some of the areas we did last year and we did some additional testing on these cells on a

synchronous orbit or a continuous over-charge, a trickle charge. May I have the first slide, Floyd?

(Slide 20.)

Well, as you remember last year, we discussed the drying-out problem of separators in general and this particular one is for the nylon where we have the 2505 and the 2505 washed out.

And this was cycled 6,000 cycles and the cell was taken out every 1500 cycles to determine the effects on the separator. I guess, for many years people know these things are drying out, but this is kind of a quantitative measurement of what was going on.

And we thought maybe we extended those dotted lines and maybe thought they would go down linearly but we have some data today which we doubt if they do that.

These cells here were cycled at room temperature, at 25 percent depth of discharge in the 90 minute orbit. They were Eagle Picher cells and they contained 26 cc. of electrolyte originally.

Can I have the next slide?

(Slide 21.)

And we did a trickle charge test on these same type of cells of Eagle Picher. There was some interest in how they operated in trickle. And we took them out at three months, six months, and nine months.

The three-month one looked about the same as the six-month. And, as you can see, there is essentially no cadmium migration, maybe a spot of two. This trickle charge rate was at the C. over 30, and at 25 degrees Centigrade.

This is the negative side of the, the side that is facing the negative plate, and all of the slides I will show on separators will show the negative side of the separator.

Now, as far as how these cells appeared when we took them out of the three, six, and nine-month eras shown on the next graph.

(Slide 22.)

These cells started out originally in absorption in g./cm.³ and that centimeter that is cubed is the dry volume of the separator, at about .72, which several cells were measured and this is the range that we got on a virgin cell.

Now, during the trickle charge period we got a different type of electrolyte change and in the cycling tests, where in the electrolyte seems to go down to a lower value of about .45 and at least at a nine-month period it stayed constant.

There was some carbonate determinations done on these cells and as far as the carbonate over the OH plus carbonate, those numbers came out to be about 20 percent and it didn't change appreciably during the nine-month test.

So, this wrapped up all of the cells that we had in that particular test, the 90-minute orbit test and so forth. This is just another piece of data that we had on these Eagle Picher cells.

May I have the next --

(Slide 23.)

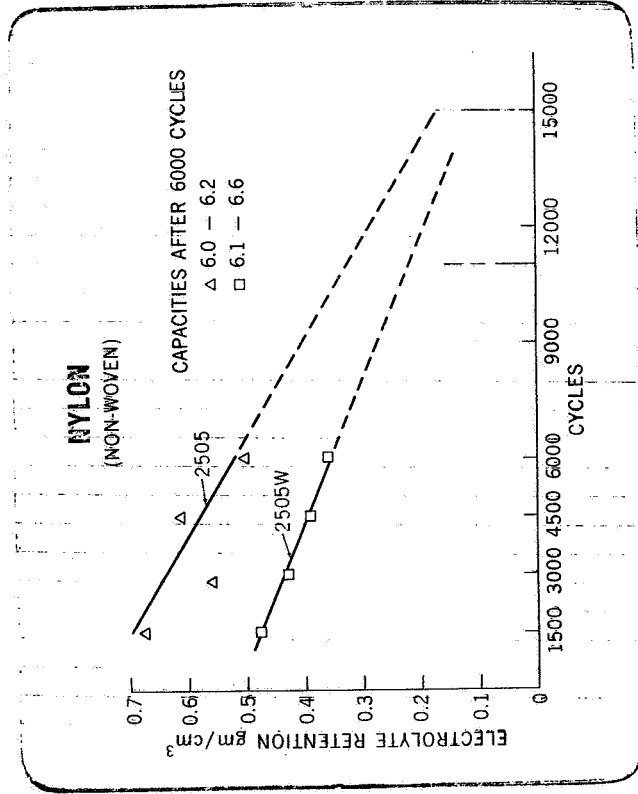
Now, many years ago we started cycling some cells with and without Teflon on the negative plates and these have, both packs have cycled about 16,000 cycles to date and this was at a 25 percent depth, at 25 degrees Centigrade.

Now, we have samples here from the virgin cells which were stored as long as the cycle test. And also a cell that only ran 11,000 cycles because it had been put in later than the others -- than the 16,000 cycle cell.

Well, the cadmium migration, you might say, doesn't look bad in these things, but most of the separator is left on the plate and especially on the bottom one where we only got pieces off.

And it was a very hard problem to get the separator right out of the cadmium or negative plate. We have -- could not get any good drawing out information on these two cycles because the separator was just putting a very thin, very dried out, but it looked like in the 11,000 cycle one where you could determine the drying out, it was about 30 percent of what originally was in the separator.

Now, remember when I say electrolyte, I mean both KOH and carbonate. Could I have the next graph, the next slide?



NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

FIGURE 20

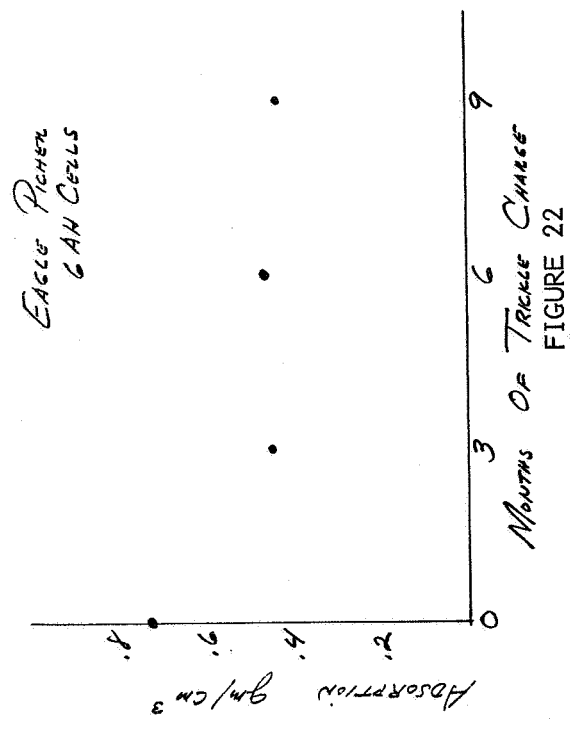


FIGURE 22

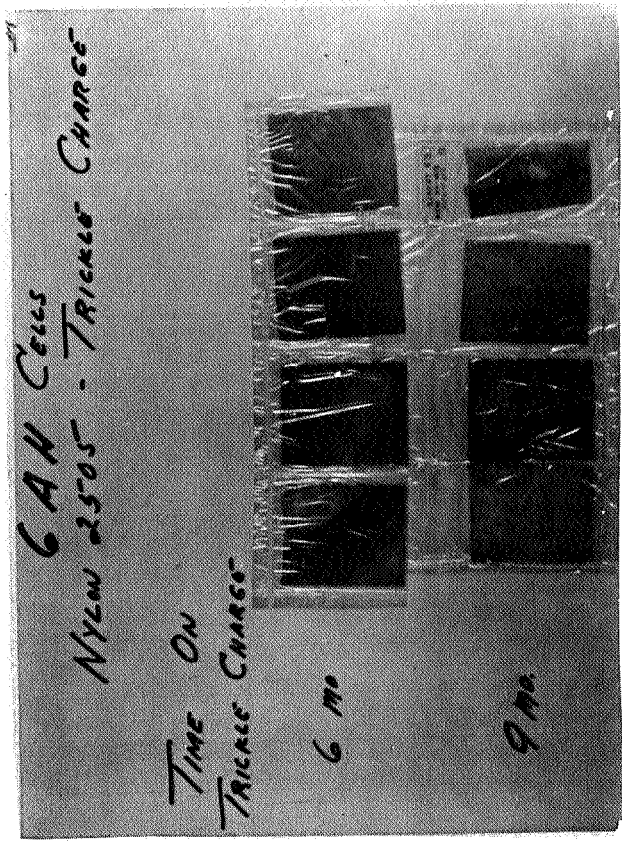


FIGURE 21

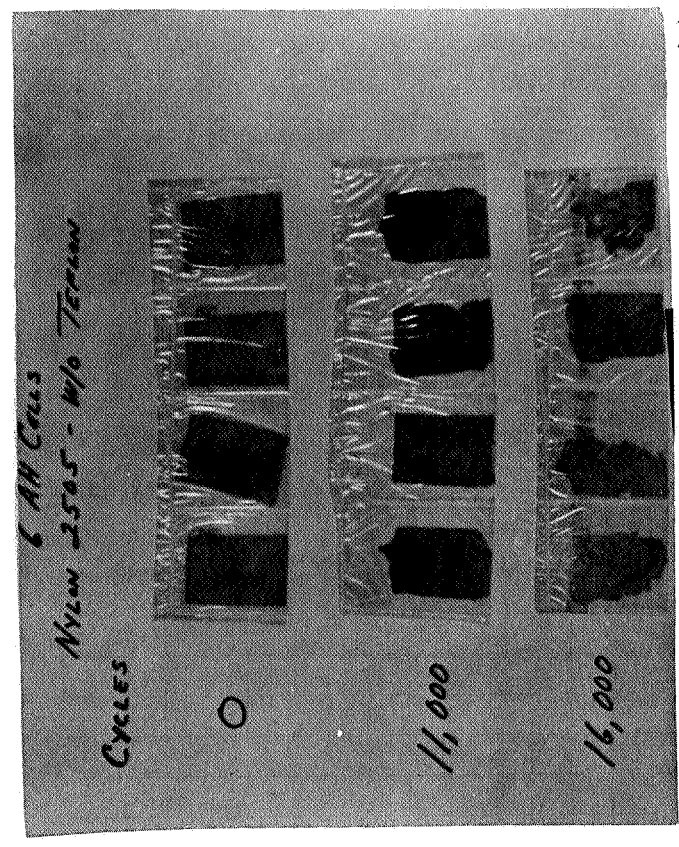


FIGURE 23

(Slide 24.)

Now, this one is of the same test, but with Teflon impregnation, or Teflon coating on the negative plates. Now, these came out practically in total, as you can see, you would see cadmium migration here that was shown last year, that might occur in about a nine-, twelve-month type of area.

These separators came away from the plates quite easily and even when they were (soxlet) extracted, there was some sticking to the negative plate, but it would come off reasonably easily.

The thickness of the separator after the test after the test was about 10 percent less than we originally started. However, these separators vary quite a bit. They can vary that much in the original lot, so I don't know if that's really a good number.

But some of it does stick to the negative plate. Now, on these three samples, we could get some effects of the drying out or the loss of electrolyte by the separator material and I have that on the next graph.

(Slide 25.)

Now, they started out with g./cm.³ of electrolyte at about .5. Now, at 11,000 cycles it was about .15 and at 16,000 cycles it was .15, so, as I mentioned before, maybe they go down linearly to start with but as we go out to some high cycle depth, we seem to be leveling out.

One thing we did here -- this was kind of a side test -- was to take two cells out at the end and recondition one. And this -- then open the cell up and look at the separator and the amount of electrolyte.

The separator cells looked essentially the same as the one that was not reconditioned, but this one here had an increase in the electrolyte content up to about .25 from .15. These packs are still running, even though the separator had deteriorated very badly in the non-teflonated cell -- it is still running but there are some indications that shorts are occurring in those cells both on the discharge and some of the cells lagging behind on the charge.

Another area that we look at and Floyd Ford talked about last year, was the storage test on cells and we took some of those and cut them open and looked at the separators

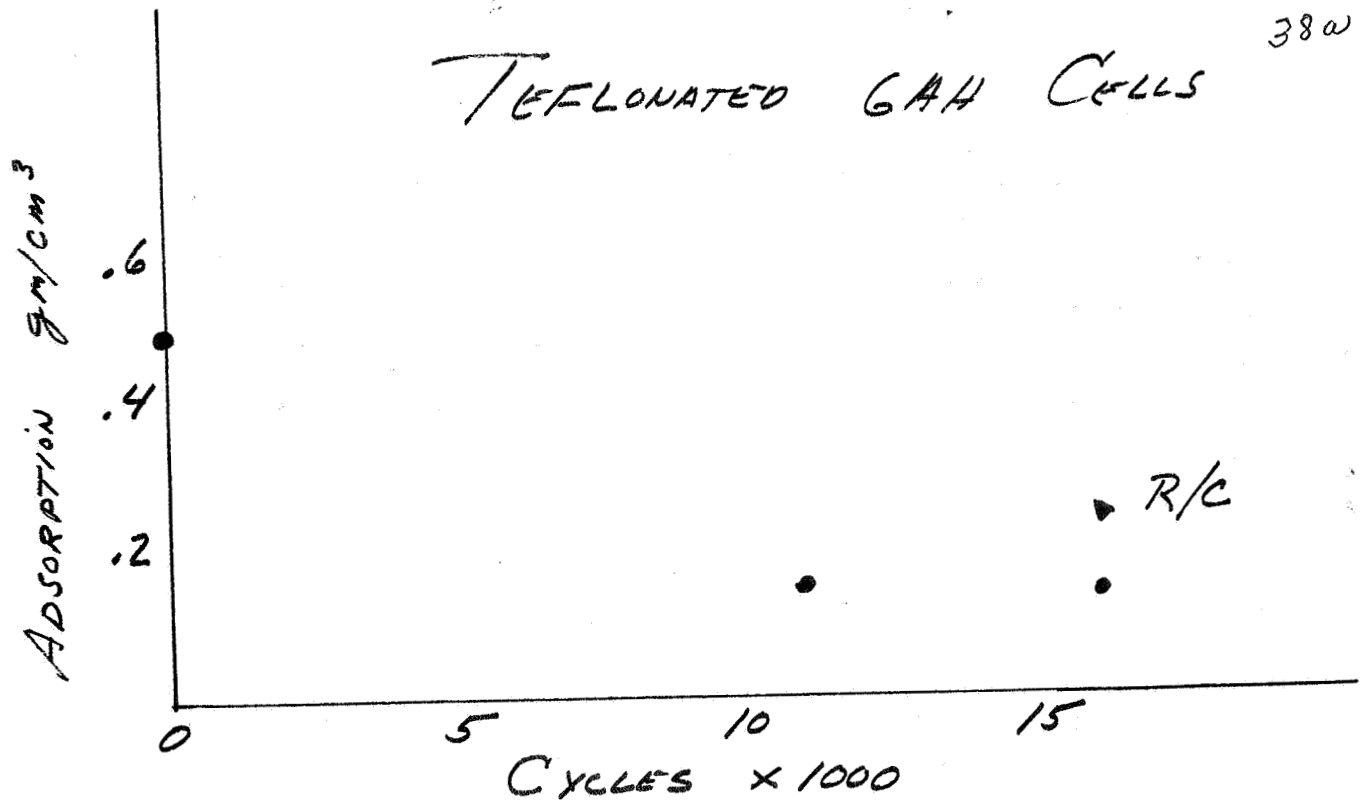


FIGURE 25

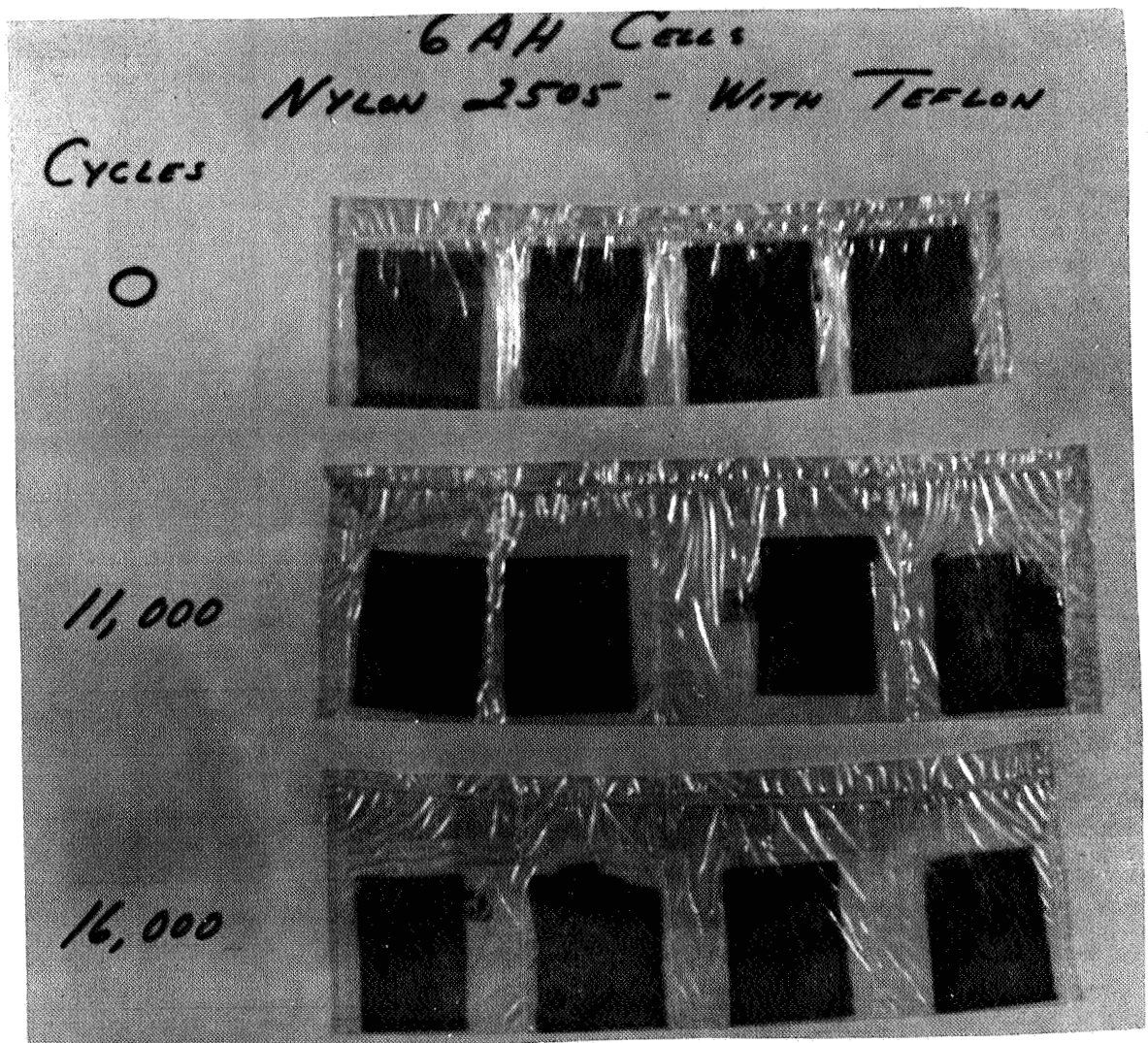


FIGURE 24

from those particular cells.

If you remember, we had a random storage test which was simulating a type of integration of a satellite. This might mean charging at various times and discharging at various depths, letting the cell sit charged/discharged/partially-charged and so forth.

We tried to simulate that operation and we've known for a long time that we'd like to change the batteries before these people fly them, especially for long-life.

There was another type of test we made which was a continuous trickle charge at C. over 30 and another test we made where the cells were stored shorted. These cells would be capacity checked every six months and this information is in the last year's proceedings.

Can I have that slide, Floyd?

(Slide 26.)

This is what the separators looked like after they came off this test. These were 20 amp/hour cells, storage test, 18 months. I believe -- they can correct me if they hear -- 66 cc. in these cells and the shorted and trickle-charged cells did not apparently have any migration as far as black areas go, where the random test showed quite a bit of cadmium into the separator but it was not going through it.

I think last year we showed a lot of data where in cycling, the cadmium migration appears to stay on one side of the separator, the difference in polypropylene separators is it appears to migrate through.

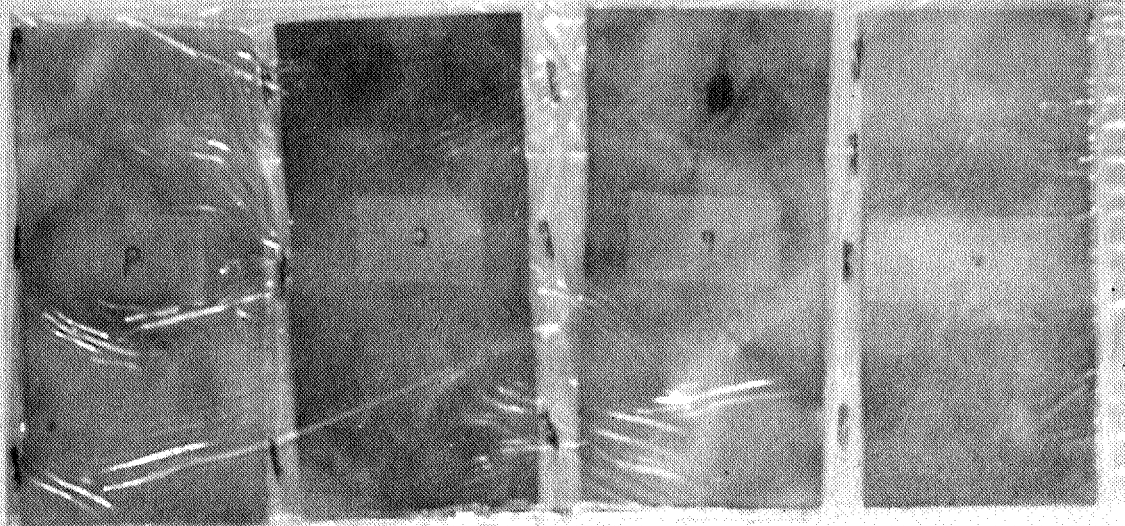
These separators were quite easy to separate from the negative electrodes. Now, we do have some drying out or electrolyte distribution information on these separators which is shown in the next graph.

(Slide 27.)

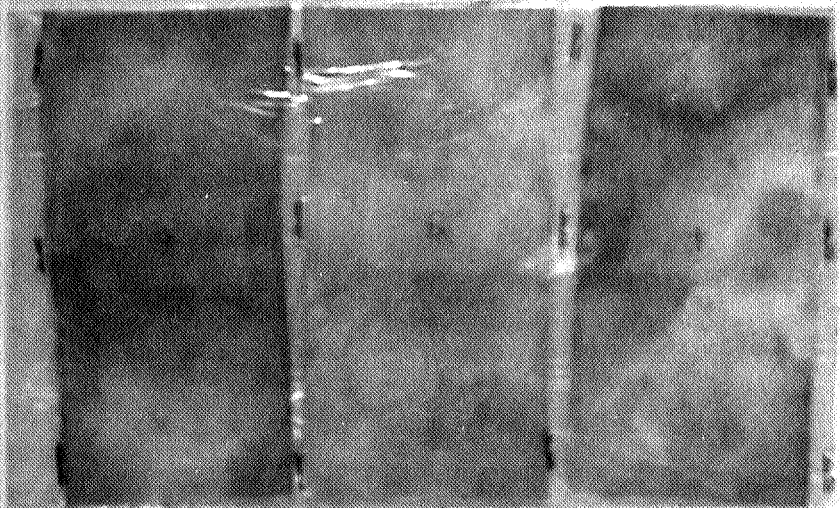
Where the storage treatment, the shorted cells had approximately, had .49 g./cm.³. This is about normal for what we find for a (Gulden) cell. We haven't got a lot of information on sixes, but one we did check a while back had about the same value, I think it was .45.

20AH CELLS - STORAGE TEST 18 MONTHS

TYPE
STORAGE



SHORTED



TRICKLE
CHARGE



RANDOM

During the trickle charge after the eighteen months, the separator had about .21 grams of electrolyte per centimeter cubed and in the random test it was essentially the same order of magnitude as the shorter test.

That's all for that one Floyd. There was one pack of cells that was kind of depleted at the (Crane), and we made it kind of standard practice to take -- when we take cells off test and out of run through this separator testing, we don't have a lot of previous test data on these, on how these cells were made. But it is a polypropylene FT 2140 and I just thought I'd show you as a matter of interest. I'm not going to say too much about this one, but these cells have gone about 16,000 cycles.

(Slide 28.)

Each pack had ten cells in it. The first pack has no failures. The second two packs -- some cells were failing below 10,000 cycles and actually these cells were, you might say, were failing at the time, but this was a piece of information FT 2140.

The cadmium is going right through the separator. If you turn them around and look at the other side, you'll see the same thing. And, especially, the lower two packs are 25 C. and 40 percent and 40 degrees C.

These -- after tests they would not pass the short test and appeared to be shorted cells. However, I'll have to admit, the 25 degrees C, 25 percent pack is still running and still maintains a fairly good capacity on capacity checks.

These are really 5 amp/hour cells, you see the 6 up there. So, I thought I'd wrap up some of these loose ends, and I say we are taking some of these cells out after many thousands of cycles. It would have been nice if we knew four years ago what to look for, to have done some analysis then, especially on this polypropylene separator.

We don't have too much information on the original virgin cells. Thank you. Do you have any questions?

Ed Kipp from Gulton?

KIPP: In relation to the absorption measurements that you made, did you also measure cell impedance, to see if there was any correlation with cell impedance with the absorption of the KOH?

HENNIGAN: Well, I know in the first lot we had a regular program in measuring impedance all along the cycling.

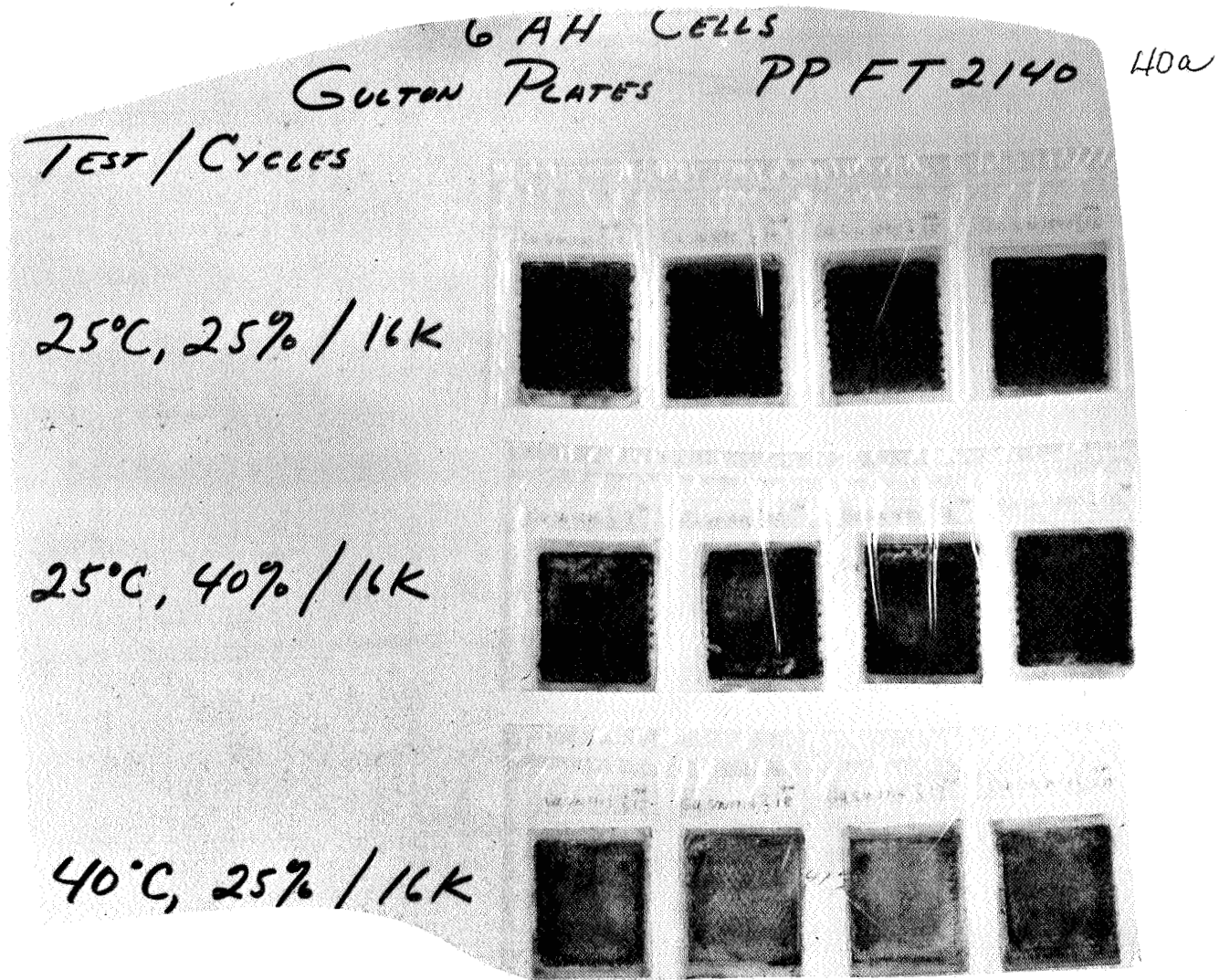


FIGURE 28

STORAGE TEST - 18 MONTHS
GULTON 20 AH CELLS

STORAGE TREATMENT	ADSORPTION gm / cm ³
SHORTED	0.49
TRICKLE CHARGE	0.21
RANDOM	0.43

FIGURE 27

For instance, on the nylon cells, there was essentially no change. It might be 3 milliohms and go to 4, go to 2 and it would just stay the same.

Last year when we ran the polypropylene cells, we noticed a two or three-fold increase in polypropylene cells because of what we assume to be was the drying out.

Earl Carr, from Eagle Picher.

CARR: Could you put the first slide up where you had the six-month and nine-month on cycle charge?

HENNIGAN: That's the second or third. You want the separator?

CARR: Yes, was there any sticking of that separator to the negative, do you remember or can you tell from the slide?

HENNIGAN: On all of these things I've talked to the people who took them out. I could say this -- when after the pack was (soxhlet) extracted and I did some separation of the separators and essentially was not sticking to the plates.

Some of the fibers are always going to hang on there, but there wasn't -- essentially the separators were about the same thicknesses we had originally put into the cells.

Do you have a question, there?

HENRY: (Telesec) When you -- on the last slide when you were showing the one's that failed, in the last two lots. When you look at the other side, were you able to see any kind of gradient or stratification across the separator material and it might be more apparent looking at the other side.

HENNIGAN: Yes, well, the reason I didn't -- I normally --

HENRY: I noticed there was a little bit up on that second one. It looks like there was a slight tendency for stratification in a vertical direction.

I'm wondering, if you look at the other side of -- take a look at the separator material, were you able to see if there were any more migration to the upper part as opposed to the lower part?

HENNIGAN: Well, one reason -- last year I showed both sides all of the time and the reason I didn't do it here was because they essentially were the same. You couldn't --

Yes, that's why I didn't bother photographing the other side at all.

HENRY: What I am really driving at is has anybody done anything with centrifusion, the effects of the satellites several feet out undergoing about 6 gs. I wonder if you are centrifuging some of the electrolyte schemes, whether we're getting any failure -- has anyone looked at that or not?

HENNIGAN: You'll have to ask other people in the audience if anybody's looked at the effects of electrolyte separators as a function of g-loading.

Dr. Griffin?

GRIFFIN: There is a lot of work on vibration testing in primary cells where you have to be very careful on vibration afterwards, after vibration testing before you use the cell. I'm certain in the Fleischer and Cooper's tests, one of things was retention of electrolytes in absorber system.

There is an A & F, AL monograph in 1964 that describes this and what happens to it. In 1968 there was similar testing, so you have some facts and figures out of there. But it's certainly -- not every structure will retain electrolyte under these conditions.

It will go out as much as 40 percent.

KARR: That's what I was wondering about. We happen to be undergoing about 11 gs. out there along the plate -- we're sitting and all of the ground testing is at 1 g. I wonder if anybody is planning to do any high g load with life type of testing.

HENNIGAN: Well, I haven't heard any requirement of that --

KARR: This is something I have been talking about individually with people. I am not getting much concern about it. I would like it to go in the minutes of the meeting.

HENNIGAN: Okay, well, thanks for your comment. I don't know if anybody's done that. I know years ago we did some on silver zinc, but it was nowhere near -- I think it

was about 1 g. or a couple of gs, I'm sorry.

Harvey?

Seiger: On the Cooper-Fleischer reference that was given, there was some separators at centrifuge of 25 g. for two minutes and there were also some positive electrodes and negative electrodes that were looked at. And most other materials held on to a good portion of the electrolyte that was first put in.

I think in some cases, twice, they spin twice at 25 g.

KARR: Are these electrolytes?

SEIGER: These are not cells. They were filled with electrolytes and put into the centrifuge.

HENNIGAN: Marty Sulkas, from the U.S. Army.

SULKAS: Tom, you had quite a bit of stuff on Teflon treatments. Have you any conclusions you have reached at this time regarding its value, whether it's worthwhile doing it.

HENNIGAN: The way to preserve the separator there was quite notable -- I mean, it avoided the sticking to the negative plate. I would say it retarded the cadmium migration because it didn't move into the separator and we could get it off and that's what normally happens -- the separator just becomes part of the negative.

I think the people from G. E. also have some information on cycling teflonated electrodes at higher temperatures. Do you care to comment on that, Guy?

RAMPEL: I think we did work for Hughes a couple of years ago. We cycled some nylon 20 amp/hour cells with various level of Teflon in the plates and also a control. We cycled it at 50 percent dod and 50 degrees Centigrade.

In photographs of cadmium migration, atomic absorption results -- some were published in one of the news reports on that work -- I believe it was the low-orbit 50 amp/hour program.

Cadmium migration was retarded almost 200-fold, at higher levels of teflon and on down.

HENNIGAN: Thank you. Are there any further questions? Jim Dunlop?

DUNLOP: Tom, I don't remember what the random test was --

HENNIGAN: Maybe Floyd could describe that a little better.

FORD: In regards to the data shown here on this slide, I think there are several important factors that may be overlooked, so I'd like to recap the results that were presented in some detail last year at the workshop. And, I think, most of you, I'm sure, have proceedings.

And you can go back and look at the electrical data at the eighteen-month time period at which this separator analysis came about. Okay, to answer your question, Jim.

The random use was to try to simulate, to the best we could possibly do, the conditions a battery would experience during integration on a spacecraft.

Now, as most of you know, integration involves a wide-range of activity -- its thermal vacs, mechanical and et cetera. We did not attempt to simulate the dynamic environment or the thermal vacuum.

But we did want to evaluate the effects of batteries, during what I'd say, the pre-test period and during the actual build-up of the spacecraft. Because, historically speaking, batteries, being one of the heaviest objects on the spacecraft, is usually put close to the center for reasons of center gravity, which usually requires they be installed quite early in the program or during the build-up of the spacecraft.

Consequently, the flight batteries were usually the first things to go in and we have test experience or flight experience where batteries were put in up to eighteen months prior to launch. And we have noticed in the over period of time, detected some very radical changes in electrical characteristics.

And this test we did, it did confirm the things that we had observed during the actual build-up and the following of batteries through a spacecraft integration period.

In summary, then, what I presented last year was I showed that the random battery could no longer be over-charged at 0 degrees C, meaning that you could not charge it if it was

c over 20, constant current, without exceeding a voltage limit -- a limit was set a 1.55, but in actuality the cells, even after six months of exposure, got up to about 1.60, which was an indicator that we would terminate the test.

There was a slight increase in the capacity of the random group. But contrasting this with the trickle charge group, there was a significant increase, and I remember the numbers in the range of 29 to 30 amp/hour capacity that these cells delivered on the eighteen-month capacity check and these cells were running like 24 to 25 ampere hours at the beginning of the test.

Now, the cells, comparing the trickle charge in the shorting condition, the electrical data other than the capacity showed very little difference, which brings you to the point that I wanted to make.

If you look at this slide and you look at the other data that he presented on the amount of electrolyte retention, I think it's fairly significant that cadmium migration, if not a by-product of trickle charging, electrolyte redistribution is a by-product of trickle charging.

So here you have two distinct cases, where you get cadmium migration without significant redistribution of the electrolyte -- and I'm comparing it to the shorted mode for a reference point.

But you get -- on the other case with trickle charging, you get significant electrolyte redistribution but not cadmium migration. And, in summary, it says that cadmium migration is related to the current density or to the state of charge of the negative electrode to some extent.

And my theory is that it is related to the current density associated with the discharge mechanism and in no way related to the charge mechanism.

Now, this is somewhat confirmed in some data that we have -- I believe it's been presented in one of the previous workshops -- I know I had the photograph on the table at one of the tables at one of the meetings for people to look at.

But from the synchronous orbit test, one of the most surprising things that we observed -- we pulled our first group of cells out -- well, actually we had a cell to fail that was a 6 ampere hour cell running at 80 percent depth and we were simulating the true (sigmus) orbit profile.

And if my memory serves me correct, it was like $4\frac{1}{2}$ years and the cell shorted, so we decided to pull that cell and do an analysis of it. In particular, we looked at the condition of the separator.

Well, what surprised us was that there was not a significant amount of cadmium migration relative to a four-year or four-and-a-half year test that we would have away from the lower earth orbit or even, you know, like the 120 or 200-minute orbit we would expect a lot more cadmium migration.

And when you look at a synchronous orbit profile, you are in trickle charge for, I think, something like 80 percent of the time -- the majority of the life of the battery you are in trickle charge.

And it's not really being discharged. So I suggest you review the legible data associated with this because I think there's a lot more there than meets the eye when you look at these figures at this time.

And, as far as the sticking, I had an experience just in the last two weeks that we opened a new cell -- the cell had gone to accept this test, as a matter of fact it's one of the flight programs.

Now, the cells had not seen sufficient test or temperatures that showed any cadmium migration. In other words, the separator was very clean. But, this was the first time I've ever opened a new cell that had a -- and granted this is relative -- but it was a very dry characteristic and there was already adherence of the separator system to the negative electrodes even though there was absolutely no signs of cadmium migration.

Now, I for one believe the cadmium migration and the related electrolyte distribution, particularly cadmium migration, is related to the wetness of the cell. And one further experience we had in this was some cells -- well, two different lots of cells made by the same manufacturer but made over a period of I guess, about a year about, again six ampere hour cells.

But we had a situation where we tested the same lot of cells in a same series string in the same test conditions. Now, believe it or not, at the end of the test, which is something like 21,000 cycle, and this is a fairly moderate or low-rate discharge with periodic pulse-type loads on it.

It was a transpondent-type satellite, to give you an idea of what the rate -- it was typically a $1\frac{1}{2}$ amp discharge

for about four hours or probably about two hours to three hours once a day. But, the thing that was interesting was that when we opened these cells and looked at the separator, there was as much difference between the wetness characteristics as day and night.

And the only thing I can tell you is those cells were made one year apart and I feel fairly comfortable in saying that if there was a difference in the amount of electrolyte those cells had, it would have probably been within the order of a couple of ccs.

You're talking about a six ampere hour cell that has somewhere around 18 to 20 ccs. in it to start with. So, I think what we're dealing with and I'll close with this -- I think I've answered your question, right -- is a very complex mechanism and there's many pieces. It's like a huge puzzle and I'm very enthusiastic that what I've heard here this morning is, at least some of it has reinforced some of my ideas and some of it has totally torn them apart.

But I think this type of meeting is a healthy environment. I think this separator situation is one that's really important to a ten-year battery.

HENNIGAN: Thank you Floyd. Do you have another question, Jim?

DUNLOP: Yes, sir, but I thank you for the answer. I don't know whether to ask another question.

(Laughter.)

You mentioned the electrolyte distribution. You did observe a lower amount of electrolyte with this trickle charge?

HENNIGAN: Yes, in both cases.

DUNLOP: Why? Do you have any explanation why?

HENNIGAN: I don't have any explanation.

FORD: Well, I'd like to reflect back on a question I asked about where the electrolyte was in the cell, if it wasn't in the separator. That's one of my theories that got blown apart this morning.

Don't underestimate the dynamic environments that that positive electrode experiences in cycling. One of the things we have seen on the synchronous orbit testing -- that

without cadmium migration as the dominant factor for life, we are finding the positive electrodes are beginning to be the limiting factor.

I think the changing porosity, the expansion and probably the change in electrode size on a cycle-by-cycle basis is causing a considerable amount of stress. You don't have really a strong electrode to start with and we start exposure to high current density. It has devastating effects on the positive.

HENNIGAN: You have a question there?

BARNETT: Would it be true that the current density across the surface of the plate would be equal and if you had a wetter surface material, you would have a lower impedance and have a tendency to have higher currents than what is placed?

FORD: Is that a comment or question?

BARNETT: It's a question.

FORD: I don't know. It sounds like a sound explanation.

BARNETT: Which is related to current density rather than dryness.

FORD: On the current density, a particular place on a synchronous testing frame are indeed cells that I think most people are aware of. But the plates were cut from a much larger plate meaning that the top and the left edge relative to the positive tear, is a coined edge.

The right edge in the bottom is uncoined. Now, there's two places where an appreciable or dissassociation or whatever you want to call the mechanism, where this is appreciable. One is, if you look at the, when you take the cells apart and you look at the edge view as it comes out and reverse it you can tell which side is coined.

On the edge view, the coined side is not denominated. The uncoined edge you can actually see the metal grid right under it. But, then, contrasting with that, the coined edge across the top, which is what I attribute to a high current density, also shows appreciable denomination from the material.

HENNIGAN: Will Scott from TRW?

SCOTT: If time permits, I have some interesting photographs and comments relating to that exact point of why the top edge comes apart, which I think you'll find very interesting.

HENNIGAN: Do you want to do it now? First, if there is any more questions, we'll finish this up first.

FORD: We planned to discuss that this afternoon.

HENNIGAN: Jim Dunlop?

DUNLOP: On the cadmium migration, did you do any analysis for cadmium on the positive electrode?

HENNIGAN: No, we did not. Will Scott?

SCOTT: Did you measure any kind of porosity or void volume in the plates that you removed from that synchronous orbit test?

FORD: No.

SCOTT: Your comments, Floyd, implied that the changes that might occur in the positive would lead to a greater porosity -- increase in the porosity. I thought that was what you were implying.

I wonder if you would absolutely measure, had measured such changes.

FORD: We did not measure the change of the dimension of the porosity of those plates in question. We did not measure the change in porosity or plate dimensions on those cells, unfortunately because of the long, of the length of time those cells have been manufactured.

We don't have any reference data to compare with anyway. The observation and the comment that I made this morning is based on the fact that every time we have had data on new plates, uncycled plates -- and I'm speaking of plates that actually where you have mechanical measurements prior to the formation of ECT test and use it as a reference or even used plates that have been through the formation on ECT test -- that we found and the program was on an CAO Program, so it would be a governed 20 ampere hour, we found that in approximately six months of cycling that each plate had increased approximately 10 percent, each positive plate had increased approximately 10 percent in thickness.

Now, on another program that I have been associated with intermittently was on the workshop battery made by EP and we found that the positive plates that they made for those batteries also show a significant dimensional change. And you're not talking about five or six years, you're talking about something that can be measured significantly in six months and I expect it can be measured significantly in probably one or two months of cycling.

HENNIGAN: Harvey Seiger?

SEIGER: I think we'll give some measurements where we determine thickening in SUS, 27 cycles. I presume we will be speaking this afternoon.

HENNIGAN: Guy Rampel?

RAMPEL: Just one comment relative to electrolyte redistribution, the drying out of the separator with time and relating that to cadmium migration, I wanted to point out that the rate of oxygen recombination is increasing and you're getting greater heat on the negative as that occurs and cadmium migration is a function of temperature and current density, current discharge.

HENNIGAN: Are there any other questions? Your name please?

WERTHEIM: (Grumman) I just wanted to know, taking into account the data that you produced last year on storage and the data you have now on storage, have you come to any tentative conclusion on which of the two storage methods, trickle charge or storage cells, are preferable?

HENNIGAN: Well, the data we had on the separator itself, the shorted cells was preferable and I think with the electrical data -- is that right Floyd?

FORD: Yes.

HENNIGAN: The data is based on that also. We had two trickle charge tests there and the separator was drying out. This appears to take away some of the life of the cell.

WERTHEIM: This bears out our initial conclusions on that, is that right?

HENNIGAN: I don't think we stated any last year. I mean, we didn't have any trickle charge data last year.

WERTHEIM: Several years ago shorted cells were considered to be best as far as storage was concerned.

HENNIGAN: I know. We're not satisfied with trickle charge. Okay.

FORD: (Goddard) I have a question rather than a comment. We are not sure what the electrolyte redistribution does for you or doesn't do for you, whichever the case may be. Because I point out that when I said earlier about the synchronous orbit test, if you look at what we know today, you have to assume there would be electrolyte redistribution in those cells.

Now, those cells are showing relative to test conditions, they are showing a decline in capacity and general performance of the cells. It's not clear in my mind, based on the data I have seen this morning (inaudible).

It's not just clear in my mind what this leads to ultimately, if you don't have to contend with the positive plate consideration or the high density.

HENNIGAN: We have a question back there. Your name, please?

SCHULMAN: On the several comments made that the cadmium migration is due to current density, does anybody know whether it's due to average current density or a pulse current density?

In other words, is it the instantaneous light current that causes the cadmium migration or is it the overall current flows?

HENNIGAN: Most of the test we have here are done at constant current discharging. There's no pulsing going on and the charged current does vary because we're using a taper-type charge. It does vary in charge.

We don't any information on what pulse would do or higher rates than we're talking about and part of the accelerator test is to really up the rates on the Ni/Cd cell and these type of -- it would be a better planned test on separator evaluation. So we may be able to answer those questions next year.

Bill Harsch from Eagle Picher?

HARSCH: I'm curious. Is there any reason why open circuit discharge storage mode was eliminated from that test?

HENNIGAN: We normally don't store cells in the open circuit discharge mode, all right, as a shorted storage-type?

HARSCH: Why?

(Laughter.)

HENNIGAN: It's kind of a practice we've come up with. I don't know if I've seen any data on -- Jim Dunlop talked about it last year, I believe, on the circuit stand.

Will Scott?

SCOTT: I will show a little data on that point, I guess, this afternoon also, open circuit discharge.

FORD: To answer your question specifically, the reason it was left out -- they were not the particular test unit included. We have planned to complement this series and that is one of the facts we want to look at.

We discharge something like a 10 percent, but my belief at this point is I am not going to get too much difference there than what I've seen on the random test because now I'm leaving the cadmium at a fairly low rate of charge.

I don't want the conclusive interpretation of cadmium migration solely related to depth of discharge. I think that gets us to an important factor.

Scott showed a photograph this morning showing a pattern of standard migration. Now, if you want to spend the time and review the probably thousands of photographs showing different cells, different types of cells and different test conditions, I'm sure you could come up with something that was a significant conclusion that the cadmium you'll find is going to be somewhat random, which leads me to believe those migration patterns as attributed to a random stress due to pressure being created at certain points within the cells.

HENNIGAN: Bill Harsch from Eagle Picher?

HARSCH: I would like to see this type of storage included in this kind of testing mainly because my personal preference of storage is discharge open circuit. However, I have no data to back it up.

The only thing I see and like is a battery that has been stored like this is much easier to recondition. We have done it, restored batteries for better than two years, open circuit discharged, and have never had any cell failure due to this kind of storage.

But there is no data to say yes or no and I would like to see more of this particular storage mode being included in some of the testing done.

FORD: Do you have the money?

(Laughter.)

HENNIGAN: Any more comments or discussion? Dr. Griffin?

GRIFFIN: Is there a difference in the volume of electrolyte, whether you have a teflon electrode or non-teflon?

HENNIGAN: There's about $\frac{1}{2}$ cc. One cell had 18 and the other cell had $18\frac{1}{2}$. The teflon had $18\frac{1}{2}$.

GRIFFIN: I wonder if the teflon would have another beneficial affect besides retarding electrolyte migration into the electrode, just from a wet-out point of view of putting a hydrophobic structure in there. I know the electrode is used to prevent that.

I am just wondering later on it would be later on to have this type of measurement on four sides. I know it's very difficult on some of these things, but I certainly think we might get some correlation here between the initial structure of the electrode, the final structure of the electrode and whether you should really have a separator in that that has a similar size at the end of some sort of gradation in size, through the separator.

One could argue you should be aiming for a structure that isn't uniform on four sides because the electrodes are changing in different ways.

HENNIGAN: Mr. Seiger?

SEIGER: How much teflon was put on each electrode?

HENNIGAN: Well, in way of thickness, this was level 1. I would rather the manufacturer comment on the thickness.

RAMPEL: Frankly, it is not a thickness situation, it's an impregnation of teflon into the electrodes and a concentration of teflon.

HENNIGAN: Dr. Goudot?

GOUDOT: Have you seen any effect of the teflon on the recombination rate of oxygen recombination?

The fabrication technique is -- as you can see -- two phases in this case. The first phase is the preparation of the flexible substrate. The asbestos is impregnated with a solution of polyphenylene oxide and chloroform.

This was necessary for two reasons: first, to give the asbestos some handlability. It's rather flexible, the (matt) is rather flexible and kind of difficult to handle. Also the polyphenylene oxide was able to coat the inorganic fibers of the asbestos and protect it from attack.

The next step in preparation is to take this impregnated asbestos, form it into a bag by gluing the edges together into which we inserted the electrodes. Both electrodes in both systems -- the silver/zinc and the nickel/zinc systems -- were inserted into this bag.

The next step is the application of a coating in this bag by dipping it into a slurry. The slurry contained two organics -- again, as mentioned, polyphenyleneoxide and a plasticizer, both of which are soluble in chloroform.

We also used some fillers, some inorganic fillers, ceramics and inorganic fibers. Next one?

(Slide 30.)

The performance we've noted with these systems in the silver/zinc, these are 40 ampere hour type cells -- this is after sterilization, after 135 degrees for about 200 hours -- we were able to obtain over 100 cycles at very deep depths. This is 100 percent depth.

We were able to obtain over 400 cycles at medium depths, 40 to 50 percent and over 1,000 cycles at rather shallow depths, 7 to 15 percent depth. Now, this was after two years of stand prior to cycling with a total wet-life of $3\frac{1}{2}$ years.

If we had cycled these cells during this three-year wet stand, we would have over 2,000 cycles and we do. We have some cells that have been cycling continuously for three and a half years.

As far as the nickel/zinc system, we have demonstrated 300 to 400 cycles at depths ranging from 60 percent to 100 percent. I must stress these are experimental cells. They happen to be three plate cells that we've built in our laboratory.

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HISTORY

PERFORMANCE

PURPOSE

- BUILD FLEXIBLE SEPARATOR TO WITHSTAND STERILIZATION TEMPERATURE

METHOD

- USE HEAT RESISTANT MATERIALS
- USE KOH RESISTANT MATERIALS
 - CERAMICS AND OTHER INORGANICS
 - PPO (POLYPHENYLENE OXIDE)
- FOR FLEXIBILITY
 - PLASTICIZER FOR ORGANIC
 - FLEXIBLE ABSORBER AS SUBSTRATE (ASBESTOS)

FIGURE 28B

Ag/Zn AFTER STERILIZATION

- OVER 100 CYCLES AT DEEP DEPTHS
- OVER 400 CYCLES AT MEDIUM DEPTHS
- OVER 1000 CYCLES AT SHALLOW DEPTHS
 - 2 YEARS STAND PRIOR TO CYCLING
 - 3-1/2 YEARS TOTAL WET LIFE

Ni/Zn EXPERIMENTAL CELLS

- 300 TO 400 CYCLES AT 60% TO 100% DEPTHS

FIGURE 30

INORGANIC/ORGANIC SEMIFLEXIBLE SEPARATOR

USES

- SUBSTANTIALLY EXTENDED LIFE OF Ag/Zn SYSTEMS
- DEMONSTRATED CAPABILITY IN Ni/Zn SYSTEMS

PRESENTATION

- HISTORY OF DEVELOPMENT
- FABRICATION
- PERFORMANCE
- COMPONENTS
- STRUCTURE
- FAILURE MODE

FIGURE 28A

FABRICATION TECHNIQUES

FLEXIBLE SUBSTRATE

- ASBESTOS IMPREGNATED WITH PPO
- IMPREGNATED ASBESTOS FORMED INTO BAG TO ACCEPT ELECTRODES.

FLEXIBLE COATING

- DIP COAT OUTSIDE WITH SLURRY
 - ORGANICS
 - PPO
 - PLASTICIZER
 - CHLOROFORM
 - FILLERS
 - CERAMIC
 - INORGANIC FIBERS

FIGURE 29

Next slide, please?

(Slide 31.)

The main thrust of my talk will deal with the structure and the mechanism. Our initial concept of the structure of this particular separator was derived from its manufacturing techniques -- the impregnation or preparation of a substrate upon which is deposited a coating.

So our initial structure was a 10 ml. substrate on top of which is deposited a 5 ml. coating. Right now we really don't know why this separator works well. It was developed empirically, but we do have some clues which I'll talk about later on.

And, also as a result of some in-house work and some contracted efforts, we have defined the structure a little bit more than this two-phase structure on top there.

Next slide, please?

(Slide 32.)

In our first investigation, our first attempt to find out what this separator is truly, we took it and broke it up into its two constituent parts, the substrate and the coating. And what we looked at here was the resistivity of this particular sample.

The full separator, this is with the substrate and the coating and its thickness can range -- well, plus or minus a ml., in this case it was 15.8 mls. -- and its area resistivity was 1.5 ohms/cm.²

The substrate, the impregnated fuel cell grade asbestos, nominally 10 mls. thick, in this case, 9.9, it has a resistivity of .5 ohms/cm.² and the cast film -- now, this was a film cast on glass of the slurry or the coating on the asbestos -- it was 5 mls. thick and had an area resistivity of .8 ohms/cm.²

Our next step in looking at this separator was to look at cast films since it did contribute a substantial amount of the resistivity to the separator.

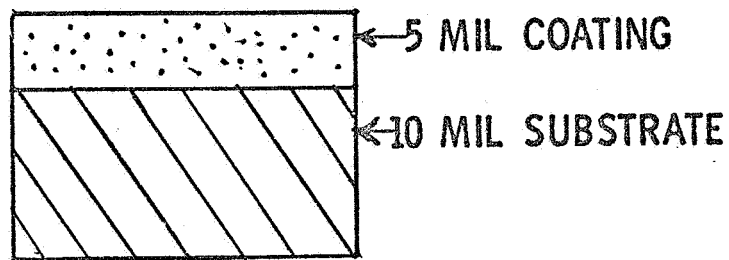
Next slide, please.

(Slide 33.)

In investigating cast films we cast a bunch of them and we varied the constituents of the film. The way the

STRUCTURE AND MECHANISM

- INITIAL STRUCTURE CONCEPT



- MECHANISM NOT UNDERSTOOD

-- CLUES AVAILABLE

- AS A RESULT OF IN-HOUSE AND CONTRACTED EFFORTS

-- STRUCTURE MORE REFINED

FIGURE 31

separator is made now the constituents contain a plasticizer, PPO, a ceramic filler and some inorganic fibers. In these films from A to G, the zero for the A film represents that the plasticizer is not present in the constituents, whereas the one underneath the PPO, the ceramic filler and the fibers means that that component was present.

Now, by comparing films A and B, the only difference is that film A does not contain a plasticizer whereas film B does. The rest of the components are the same. The PPO is present, ceramic and inorganic fibers.

As we notice the absorptivity of 45 percent KOH decreases drastically when the plasticizer is removed as in film A the absorptivity is less than 10 percent and the film B, it's over 35 percent.

The resistivity, the volume resistivity drops drastically when we add the plasticizer from 630 ohms/cm. for film A to 60 ohms/cm. for film B. The same type of conclusion can be gotten from comparing films C and D.

Again, all the constituents in films C and D are the same, except film C does not have a plasticizer and film D does. The absorptivity of KOH drops from 20 percent with the plasticizer to less than 10 percent without the plasticizer and there is also an increase in the resistivity from 180 ohms/cm. for a film with the plasticizer to over 650 ohms/cm. for a film without the plasticizer.

So, by comparing these four films, A to D, we say, well, the plasticizer is important. Okay, let's drop everything out and see what kind of film we can get if we just use the two organics, the plasticizer and the polyphenyleneoxide.

So we cast a film with that and to our surprise -- this is film E -- and to our surprise we found the absorptivity to be rather low and the resistivity to be extremely high. Evidently, something else is necessary.

So, looking at films D, E, and F, we can say that if we have the plasticizer and the PPO in film D and we add the ceramic filler and compare that to film E which does not have the ceramic filler, we notice a drop in the resistivity from 1,000 to 180 ohms/cm. for the film with the ceramic filler.

The same type of conclusion can be obtained by using film F and comparing it to film E. When we added the inorganic fibers the resistivity drops from over 1,000 ohms/cm. all the

way down to 40 ohms/cm. For completeness we also cast the film G, which is just the pure polyphenyleneoxide. It had essentially no absorptivity and an extremely high resistivity.

So, our conclusion is that plasticizer is important and we need something else. We wanted to find out why film E had such a high resistivity and film F didn't, so we used the scanning electron microscope -- next slide, please --

(Slide 34.)

-- in which we took these appropriate films and fractured them and looked at them at a 45 degree angle. Now, in this photograph, this is the surface of the film and this is the interior of the film.

The film contains PPO and the plasticizer only and as you can see it's rather cellular in structure in the interior blind pores and therefore you can postulate why the absorptivity was low and the resistivity was rather high.

In the next viewgraph, this is a film containing the inorganic fibers, plasticizer and PPO. Again, this is a fractured film again, the same type of arrangement. Again, we see the cellular structure.

(Slide 35.)

It's much smaller and we do see some inorganic fibers permeating from one cell to another and this probably gave us the rather high absorptivity and rather low resistivity.

Okay, from this we're saying that the plasticizer is rather important. But besides that we also need something to break up the cellular structure, whether it's the ceramic filler or the inorganic fibers or any other mechanism.

Okay, the next viewgraph.

(Slide 36.)

Here, we're starting to look at the completed separator. This is the coating. This is looking face-on to the coating which is on top of the asbestos and what we saw using the scanning electron microscope was a rather continuous film in which you can see imbedded the ceramic filler and the inorganic fibers going along here.

COMPLETE SEPARATOR AND COMPONENT PROPERTIES

SAMPLE	THICKNESS,		AREA RESISTIVITY AT 18° C; 45 W/O KOH, Ω -CM ²
	MILS	CM	
FULL SEPARATOR	15.8	40×10^{-3}	1.5
SUBSTRATE	9.9	25×10^{-3}	.5
CAST FILM	5.0	13×10^{-3}	.8

FIGURE 32

CAST FILM OF PPO + PLASTICIZER

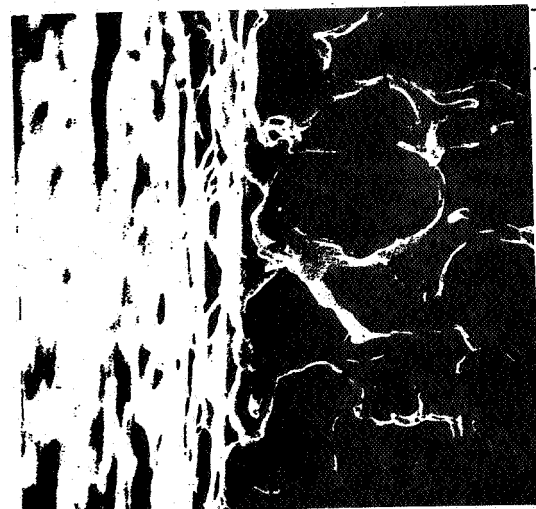


FIGURE 34

1 μ

CAST FILM PROPERTIES

SAMPLE	CONSTITUENTS				45 W/O KOH	
	PLAST	PPO	CERAMIC	FIBERS	ABSORPTIVITY, V/O	RESISTIVITY AT 18° C, Ω -CM
A	0	1	1	1	<10	630
B	1	1	1	1	35	60
C	0	1	1	0	<10	650
D	1	1	1	0	20	180
E	1	1	0	0	<10	>1000
F	1	1	0	1	50	40
G	0	1	0	0	<10	>1000

FIGURE 33

CAST FILM OF PPO + PLASTICIZER + FIBERS

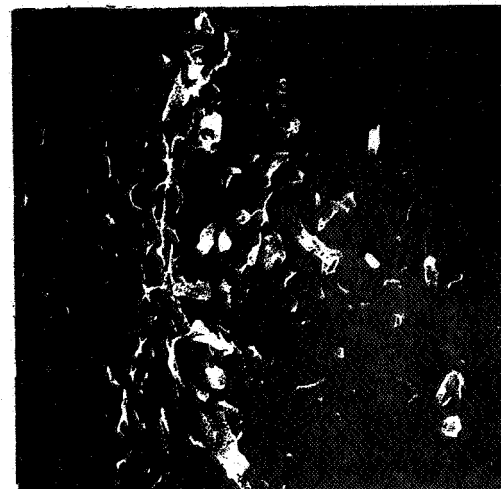


FIGURE 35

1 μ

58a

One interesting thing we noted is that we did find some holes that actually penetrated into it and we could see the ceramic fillers on some of these and the inorganic fibers. Our question was: how deep do these holes go?

(Slide 36a.)

So, again, we took the thing, fractured it and looked at it with the scanning electron microscope and the next photograph was rather revealing and surprising. This, again, is at a 45 degree view of a fractured coating and the surface, which we saw in a previous slide, as you can see, is very, very thin.

Underneath the surface -- this is the pleated surface -- underneath the surface we have a very porous region where we can see the ceramic filler, where we can see the inorganic fibers -- and not shown through here -- you can see there is an organic web holding these inorganic fibers together.

Next slide, please.

(Slide 37.)

This is a cross-section of a separator that was mounted typically and polished and then we took a picture of it. In this case, this is the coating, the slurry, and this is the fuel cell grade asbestos substrate.

This here is the mounting for the particular sample. The past two slides we've dealt with the surface, the very thin surface up here which is impervious and it does have some holes in it and the major portion in this region which is the inorganic material held together with by an organic web.

What we haven't looked at or talked about yet today is what is the interface between the coating and the substrate, what does it look like and what is the structure of the substrate. You'd expect that since we applied the coating on a rather porous substrate that there would be some penetration.

And, from this we're speculating that if there is any penetration of the coating into the substrate, it probably is the organic part of the slurry, the plasticizer and the PPO.

We also noticed that when we take this separator and expose it to KOH and allow it to expand freely, it splits right down the center of the substrate.

We wondered why the heck this happens, but it turns out in the impregnation technique, in the preparation of the substrate, when you coat the substrate, the PPO does not penetrate totally into the substrate. It remains on the surface, coating the asbestos fibers on the surface only.

SURFACE OF SEPARATOR

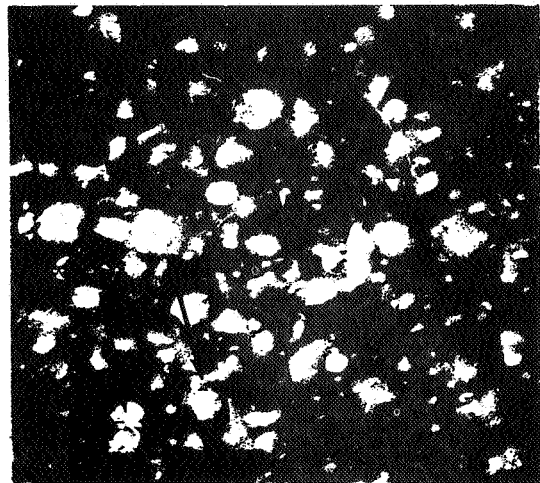


FIGURE 36

10 μ

45° VIEW OF FRACTURED COATING
OF COMPLETE SEPARATOR

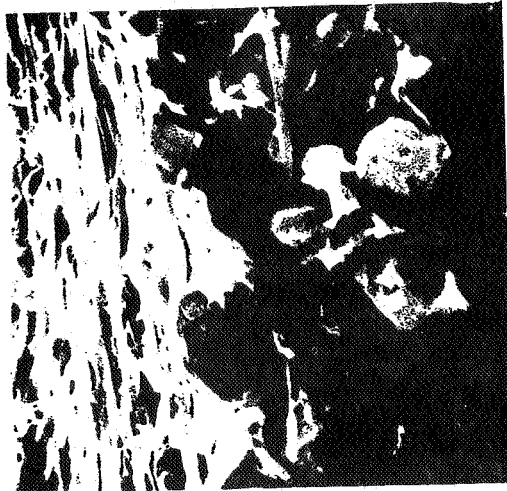
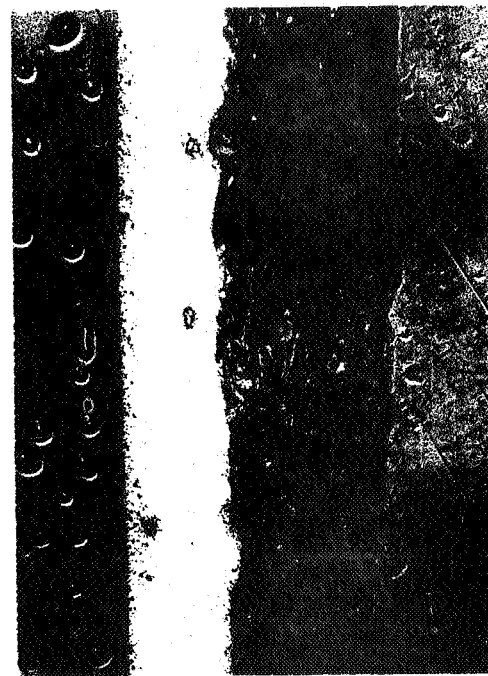


FIGURE 36A

1 μ

CROSS-SECTIONAL VIEW OF MOUNTED AND
POLISHED COMPLETE SEPARATOR



COATING

SUBSTRATE

100 μ

FIGURE 37

Next slide, please.

(Slide 38.)

So, to summarize, this is what we think the structure is, it's no longer two-phase, it's no longer very simple. We have the coating, again, and the substrate. The coating contains a skin or cuticle or whatever you want to call it that has some holes in it.

Underneath it is a rather porous region of the inorganic material held together by, inorganic material held together by an organic web. Then, an organic penetration region into the substrate, the substrate, the center portion of the substrate lightly impregnated asbestos and/or pure, raw asbestos and on the bottom part, the PPO coating, the asbestos fibers.

We just recently tried to determine what the composition of this penetration region was, so we used the IR spectrometer and we found out to our surprise that it is organic, but that it contains a lot of plasticizer, not very much PPO.

So it looks like in the penetration region there is some fractionation. We want to look deeper into this penetration region and that's what we're doing to try to find out whether or not the deeper you go into the penetration region close to the surface -- from here to here -- whether or not you find less and less plasticizer and more and more PPO.

Also we want to find out what the composition of the skin is. We think it's composed of the plasticizer and the PPO, but we're not sure.

Okay, next slide, please?

(Slide 39.)

Now, this is the failure mode. The silver/zinc system using this separator -- when the silver/zinc cell fails, it fails by penetration, catastrophic shorting of a zinc nodule, not a zinc dendrite, an actual zinc nodule.

It's rather large, something like one, two or three millimeters in diameter. And, in looking for this short, you have to separate the two bags and the nodule will stick to either the zinc bag or the silver bag.

In this particular case, which is a cross-section of this nodule, the nodule stuck to the silver bag. This is,

this region in here is the silver separator, this is the asbestos and the coating. The zinc separator is the asbestos for the zinc separator is over here and you can see the coating existing right here.

It looks like the zinc nodule, from the zinc electrode, grew out into the asbestos, tried to find the place where it could penetrate the coating, found it, spread out again, looking for a way to penetrate the silver coating, found it, penetrated the coating for the separator on the silver electrode and then spread out and actually touched the silver electrode.

We looked at this nodule using x-ray diffraction and scanning electron microscope with the (EDX), energy dispersive x-ray. We found out that in this region, surprisingly, it's dark -- among other things -- this region is dark and you would expect it to be white.

We found a lot of elemental silver in this region. We also found in the nodule, there is some silver, not much, but there is some and it's all zinc. We found zinc in this region and we also found zinc up in this region, obviously.

Next slide, please?

(Slide 40.)

As far as the on-going investigations, we both have in-house efforts and also contracted efforts and we're looking at diffusion -- we're running some diffusion tests for silver complexes, zinc complexes and KOH.

We're also running retention tests for the silver species. We're also running various conductivity tests, trying to find out what makes the separator tick, the composition of structured layers -- as I mentioned -- we want to find out what is the composition.

And we're also interested in when the separator is it effective -- either aging or use effects. I must add that we're also working quite heavily in making the separator a little bit more flexible so we can wrap it around the electrodes and we are also working on mass-producing this separator.

The way it's built now, it's a hand operation, expensive, slow, but we are working on mass-production techniques. Thank you.

HENNIGAN: Do we have any questions for Mr. Bozek?

COVER: (GAF) What asbestos fiber do you use?
Could you give me more detail on that?

CROSS-SECTION OF MOUNTED AND POLISHED NODULE

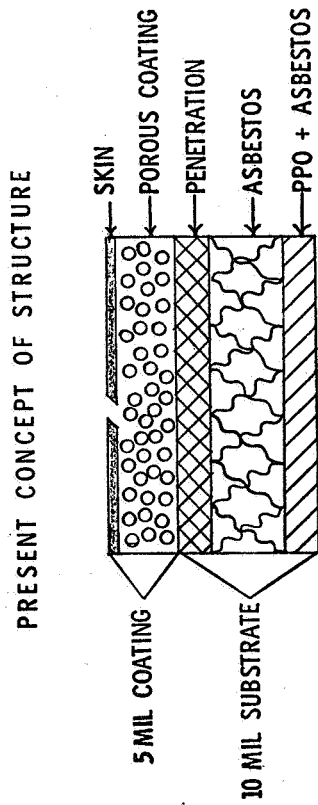


FIGURE 38

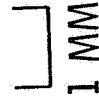
ON GOING INVESTIGATIONS (IN-HOUSE AND CONTRACTS)

- DIFFUSION TESTS
 - Ag, Zn, KOH
- VARIOUS CONDUCTIVITY TESTS
- COMPOSITION OF STRUCTURED LAYERS
- AGING AND USE EFFECTS

FIGURE 40



FIGURE 39



BOZEK: It's regular fuel cell grade asbestos which you can obtain from the Johns Mansville people.

HENNIGAN: Mr. Griffin?

GRIFFIN: Wasn't there some problem with the system of gassing in KOH and also wasn't there an impurity problem of ion with the asbestos fiber? How do you go around these two problems?

BOZEK: Well, this was gotten around by impregnating the asbestos with polyphenyleneoxide and evidently it's working because we're not getting any gassing problems. There was some, I guess, iron in the asbestos and we tried to coat the asbestos fibers with the polyphenyleneoxide. Did I answer your question?

GRIFFIN: I was wondering on a long-term effect which, you know, why people are here, the next question is how does this apply to nickel/cadmium system? Do you think this system has enough air permeability for it to fit into a nickel/cadmium system?

BOZEK: I'm not a nickel/cadmium man, so I can't answer that, I'm sorry.

HENNIGAN: We did measure the air permeability of this material and it just doesn't pass much air. It's very slow. Something will have to be done to it to make it more porous. Steve Gaston of Grumman?

GASTON: Do you have any electrical performance information, let's say, in the silver/zinc cell, what it looks like in the separators like, the voltage characteristics, what they look like, whether the high density profiles look like?

BOZEK: Yes, there are some contract reports out, one by Al Himy, when he was with the Astropower people. I think it's CR-1812 and it will give you some performance characteristics. And the other one is a final report from the Stanford Research Institute under Dr. Smatko, was just released a few months ago and he does have performance on the cells that are on test over there right now. These are 40 amp/hour silver/zinc cells made originally at the Astropower facility many, many years ago.

HENNIGAN: Jim Harkness of Crane?

HARKNESS: You said on your cycling you were running 100 percent depth of discharge cycle. Were you running

a C over two rate and getting 40 amp/hours per cell?

BOZEK: The question is what is 100 percent. I guess people consider 100 percent the formation capacity. We're not getting the formation capacity out at a C over two rate. We're getting around 75 percent of that.

HARKNESS: Are you running a two-step discharge?

BOZEK: This is a constant -- no, it's constant resistant discharge. It's not a constant current.

HENNIGAN: Sam Bogner, JPL?

BOGNER: Are you running any control cells with other types of separators?

BOZEK: I guess the only thing we can consider a control would be a similar cell using the SWIGX separator. I wouldn't consider a control, but it's operating on the same regimes and it was initially, the cell was initially built to test the GX material as to its applicability to the silver/zinc system and it is performing well.

I have no data and there is data available. If you'd contact me, I'd certainly try to get ahold of it for you. But that is about the only control that we're running right now.

HENNIGAN: Aiji Uchiyama?

UCHIYAMA: In your experimental cells, you indicated these were nickel/zinc cells?

BOZEK: The nickel/zinc. Yes, the experimental were nickel/zinc cells.

UCHIYAMA: Okay, well, in the silver/zinc cells, what was the ratio of the positive to negative?

BOZEK: I can't answer. I really don't know. I think something like two to one sticks in my mind. There is twice as much zinc as there is silver, initially, am I right? Okay.

UCHIYAMA: What was the answer?

BOZEK: Two to one was the ratio between zinc to silver -- twice as much zinc as there is silver.

HENNIGAN: Marty Sulkes?

SULKES: Have all these separators in your latest cells been sterilized?

BOZEK: Some of them have been and some of them have not been sterilized.

SULKES: Do you find you have to give them a sterilization treatment to get the resistance down?

BOZEK: No, we find that you have to heat treat them to get the -- well, to get the capacity in. The sterilization temperature is not necessary, but we ran it because in the test, the viking mission required sterilization, so we did run it.

HENNIGAN: Bob Steinhauer?

STEINHAUER: What form is the PPO that ends up next to the silver plate?

BOZEK: In what form is it?

STEINHAUER: You know, in fibers or is it a --

BOZEK: No, PPO is in a solution initially and the substrate is then impregnated with this solution and the solution evaporates leaving the PPO.

Now, I don't know whether it's coating the fibers, or it's a sheet -- I really couldn't say.

STEINHAUER: Is this the main thing that restricts your permeability or air flow?

BOZEK: I really don't know. The air flow may be a function of soak times, it may be a function of how the separator is used. If I were to make a guess, I would say that the air flow is probably restricted more by that coating on the surface, that skin.

HENNIGAN: We have to get to lunch at 1:00 and maybe we could continue this discussion after lunch and we did have one more short comment by John Perry on the inorganic separator, is that right?

And we'll start with that after lunch. We'll go out the back way here. Some of the people from Goddard can lead the way. We will be back at 2:00.

(Whereas, the proceedings recess for lunch at 1:00.)

AFTERNOON SESSION

(2:00 p.m.)

HENNIGAN: Could we have everyone come in, please, so we could start the afternoon? We still have a few more tickets for the cocktail party and we're still going to go for three bucks. '3:00 the prices goes up.

We have one additional speaker on separators and it's more or less related to the talk that John Bozek gave this morning. Is Mr. John Perry, or Dr. John Perry here from Arthur D. Little, inorganic separators for alkaline batteries.

PERRY: Thank you. At 9:00 o'clock this morning, I didn't know I was going to be standing here, so this is not a formal presentation but a brief summary of the work which we're doing under contract to NASA/Lewis with these inorganic separators.

What we've set out to do is to try and explain the mechanism by which these separators work, to try and explain why they perform better than the (cellophane), the sort of cycle life is concerned, and I think the prime area that is of interest or has been of interest to us in the last few months, has been explaining why they are effective, so the diffusion barriers.

I think the principle point about these separators is they do succeed in preventing silver migration. This gives the extra life compared to (cellophane) without providing a very much greater resistance to the cell.

And I think if one was to look and figure merit for silver/zinc separators, one ought to compare these two factors, the silver barrier capability and the conductivity. So we set out to try and explain why these separators are effective in preventing silver diffusion.

The first point that we considered was that the inorganic component could operate in some way as an ion exchange material. The ceramic component which John Bozek didn't mention this morning, is a defect oxide and does have a surface negative charge and the point that occurred to me was that perhaps this surface negative charge is capable of picking up the few silver, soluble silver species that occurred in solution.

Now, despite the fact that they do occur as negative ions, I think that the reverse of the contracts in process could

occur for absorption of the silver on the surface. So we looked initially for evidence that the inorganic component did show some ion exchange capabilities. The first point we examined was the pH of the slurry of the ceramic powder and one does find that it does behave as a sort of a weak acid and produces a basic solution when mixed with water.

That seems to indicate that the surface is absorbing hydrogen ions and liberating some hydroxyl ions in solution. The pH shift is rather to be small. It's just a unit and a half or so.

But there is an indication that the surface charge is present. Also we did some zeta potential and electrophoretic velocity measurements and this does confirm that the surface does have a negative charge.

But along with these measurements we were starting to carry out conductivity and measurements of diffusion of KOH. We were doing these measurements as a function of temperature and concentration.

And the surprise to us was the extent to which the separator interacted with the electrolyte, the amount of the plasticizer that we were able to leach out and the changes in conductivity and diffusion rates that occurred after these separators had been pretreated to elevated temperatures, not necessarily corresponding to sterilization but at least 80 degrees Centigrade for several hours.

So this generates the other possibility that what we are doing is generating microporous membrane or some other form of membrane inside. So we started looking at the concepts involved in situ.

And I think that the main point to come out of the measurements that we've made is that the possibility that what we're doing here is in the dipping process in the manufacture of the separator, we are creating a skin on the surface of the coated layer that John Bozek showed this morning and that this skin constitutes a microporous membrane that is thin enough to have good conductivity but is, nevertheless an effective value for the diffusion of the silver.

I think one of the interesting points that's come out of the results is that if we look at two of these separators together in the configuration in which they exist in the cell and compare the diffusion rates of potassium hydroxide and silver ions by radio tracer techniques through one separator and two separators, the diffusion rate is cut by a factor of

five for the two separators, not the factor of two. If we look at the same effect in conductivity, putting two separators touching each other, we see exactly double the resistivity, so there are two different mechanisms occurring here.

I think in diffusion there is significant diffusion through flaws, pinholes, cracks in this thin skin on the outside of the coating, which effectively -- when you put two separators together you cut down the rate of diffusion through these defects -- but the conduction mechanism is not affected by doubling up the separator.

In other words, we have something of a special conduction mechanism here. I would suggest that the principle conduction is by hydroxyl ion. You would expect the transfer number to be very high in the concentrated electrolyte anyway.

It looks as if we have this in the membrane as well. But, as ever, we did one experiment too much and we do observe a cation effect as well. The conductivity varies if we vary the cations, so we have something still of a problem to explain here.

But that's about the situation we are at the moment with this program which is still in progress. Thank you.

HENNIGAN: Are there any questions for Dr. Perry?
Charlie Palandati?

PALANDATI: Actually my question is to Mr. Bozek and not Dr. Perry. About a year and a half ago we had a test program in conjunction with NASA/Lewis in HS-40-7. It looked like we were looking at problems on the cells after approximately 20 or 30 cycles in a synchronous orbit.

But the cells were no longer capable of delivering the rated capacity at the high current rate, in this particular case, C over two or 20 amps. We couldn't get any more than 18 or 19 amp-hrs.

Six months later when we went into the next period we also found again we could no longer get the 40 ampere hours out again. We were no better than about 18 ampere hours. At the same time NASA/Lewis was running a test similar to ours and they had it showing the same thing.

The only way they could get the capacity out after a while was by dropping the discharge rate down to 2 amps. I was wondering whether -- I know NASA/Lewis did receive the cells back -- I was wondering when they went ahead and tore

the cells down as to whether they found out anything in regard to electrolyte concentration, dryness of plates, separators and so forth.

BOZEK: I really don't know if I could answer your question. We did have a problem with the Crane cells. The problem, I think, was in the charging and the voltage limit that was used in a charging cells, when we charged them.

I think -- if I'm -- they were overcharged a little bit, considerably overcharged and this may have contributed to their short life and their capacity -- you're gassing, you're drying out, you're doing things that you don't want to do with the silver/zinc cell, when you overcharge them.

PALANDATI: I think Bill Nagel also saw on his test where he ran one cycle a day. At the end of 100 cycles, he was only able to get out 18 amps, at the end of the first hundred cycles.

At the end of 200 cycles, he also again could not get the nominal 40 amps out. It was somewhere in the neighborhood of 20 amps.

BOZEK: Was this at 100 percent depth you're talking about?

PALANDATI: 50 percent depth, one cycle per day.

BOZEK: I'm not familiar with that work. At 50 percent depth, we have demonstrated 400 cycles. Now, these may have been cells that were cycled when the testing apparatus was not capable of limiting the charge, the amount of charge by voltage limit.

This may have been the case. I'm not sure, I'm not familiar with that one.

PALANDATI: On the voltage, what would you recommend as being a good voltage limit for those particular size cells?

BOZEK: I can answer that by saying that it depends on the type of separator you use and who makes it. The 40 ampere hour cells that were made at the Astropower Laboratories and are being tested right now, two volts and something below that like 1.99 -- if you consider that being below -- would be a good limit for that particular, for that cell that was built by Al Himy at the Astropower Laboratories.

If over people use different dipping techniques or coating techniques, you may find that you have to reduce or

maybe increase the voltage limit because of the IR drop in your separator, but at this particular separator, two volts seems to work very well for us.

HENNIGAN: Marty Klein, do you have a question for --

KLEIN: Yes, on the mechanism of stopping silver -- I'm not sure I understood -- you think the inorganic material is actually a silver sponge and absorbs the silver?

PERRY: I thought this was a possibility initially and we did some experimental work to try and establish that. The measurements we've done with silver retention since that time indicate that the amount of silver that's picked up by the ceramic is insignificant compared to the amount of interaction of the organic component of the separator.

I was somewhat limited in time and I didn't get through to telling the whole story, but we've done some silver diffusion/silver retention measurements that I didn't mention.

And we find that there's a significant interaction with PPO and particularly with the plasticizer and I think this does very much more in the way of providing a chemical sink for silver than does the ceramic component.

The hope is that the ceramic component might be reversible. In other words, it would pick up the silver on charge and then on discharge is the -- the amount of complex silver ion in solution decreases, it could come back off the inorganic component and plate out.

KLEIN: Is that true though?

PERRY: We haven't done enough work to find out whether that's true or not. This would require a very long term experiment. We're just starting with now with some exercised membranes.

These are membranes that have gone through I think 1,000 days of operation on stand and on charge and they pick up a lot of silver. I want to see now whether the inorganic component can contribute to the pickup of silver.

HENNIGAN: We have a question from Ron Haas, Philco-Ford.

HAAS: I think I understood in the previous presentation that the primary failure mode, or as I interpret it, the

only failure mode of this particular separator is a zinc penetration and it is not felt that a silver one is -- what's your feelings?

PERRY: Well, the failure mode is zinc penetration because the separator effectively stops diffusion of the silver and we set out to explain that in the first place.

HAAS: One other question, then. If we were dealing with a cell in which there was no zinc or cadmium present, what would be the failure mode of that particular cell, separator-wise?

PERRY: I presume we're talking about silver hydrogen that --

HAAS: Yes.

(Laughter.)

PERRY: I think you could effectively contain the silver to give you a very good stand or cycle life. If you want to guess, I suspect that you'll either flood out or dry out your hydrogen electrode. Jose Giner?

GINER: Could you explain the silver retention by the fact that the separator is very thick and you don't have convection? Simply by fixed flow, it should be very low due to the low concentration of silver in the solution.

PERRY: This is a possibility. We do see a difference in looking at silver diffusion through these separators by inverting the position with respect to the high concentration of silver.

You know, these are not isotropic separators. They start off with this coating, which I think has a thin film in front of it, then the ceramic which is held in place by the organic component.

Then you have the asbestos which is being coated with PPO. So the asbestos, I think, is a reservoir in the cell operation containing the movement of electrolyte in the cell and certainly it does immobilize to a great extent the electrolyte that it contains and this could reduce the amount of diffusion of the silver.

We are sort of slicing up these separators at the moment in looking at the diffusion rates through the various layers of the separator to see what effect this might have.

HENNIGAN: Well, that concludes the session on seals and separators and this afternoon we'll continue with storage experience and manufacturing developments and in this session Floyd Ford will be the Chairman.

FORD: Thank you, Tom. The arrangement of the speakers the rest of the afternoon, first, will be in the storage and effects of storage reconditioning. Then we'll move on into the area of materials for manufacturing as far as impregnation, centering and then we'll move on into the analysis area and if time permits we will probably get on into some of the areas related to testing.

And the reason I wanted to bring this up is that I have several cards here that we probably won't get to today, but we will plan to pick them up first thing in the morning.

We have three discussion relative to storage effects. The first one is Mr. Stan Krause of Hughes Aircraft Company. The subject is Storage, Reconditioning Test Methods During the Non-eclipse Periods. Stan Krause, please.

KRAUSE: Good afternoon. Hughes Aircraft Company started to run some long-term storage tests in 1969 on 15 amp/hour General Electric cells. The system application at that time was for INTELSAT4 and you'll find that what we call the various storage modes are somewhat applicable to that system -- the charge rates, discharge rates and that sort of thing.

And unfortunately, they won't fit everybody else's system or some of the other tests that have been run. However, when I talk about storage and storage reconditioning we are discussing the period for synchronous orbit spacecraft in which there is a sun season of approximately 120 to 130 days between eclipse seasons -- twice a year.

And, although the batteries have to remain active and perhaps at certain times support the spacecraft in the event of failures and power required to clear shorts and/or operate other devices, it really is a storage period that is quite critical to the long-term operation of the spacecraft.
(Slide 41.)

I think the first viewgraph summarizes the five different types of storage modes. You'll have to excuse our Publication Group, they're very enthusiastic and these colors are very exciting.

We have five five-cell battery packs in this test, each of which went into a particular kind of storage mode. Pack No. 1 was essentially open circuit storage in the charged

condition for 120 days at a time and it was periodically top-off charged at approximately C over 36 for 48 hours, every 30 days.

There were some small loads on the battery which simulated telemetry and certain charge regulator diodes that hang on the battery on the spacecraft, so it's not really and truly open circuit storage, but closed.

In any case, Pack 1 was simply charged every 30 days, just topped up for 48 hours. Pack No. 2 also had telemetry loads, however, every 30 days, at least starting into the -- this is a real time test by the way -- every 30 days starting into the, after the third season, it was cycled. It was charged for 48 hours, discharged all the way down to around 1.1 volts per cell and then recharged again and left that way for another 30 days.

The third pack also had telemetry loads, however, that was placed on a continuous C over 36 charge for the entire 120 days storage period. Pack No. 4 was also placed on continuous C over 36 trickle-charging continuously and the difference between Pack 3 and Pack 4 is that prior to the start of each simulated eclipse season, Pack No. 4 was reconditioned by deep cycle and a recharge.

Pack No. 3 was not reconditioned before an eclipse season, it would just simply go right straight into the first cycle of the eclipse season. Pack No. 5 would be discharged down to around 1.1 volts per cell to a very, very low state of charge and then just simply allowed to stand open circuit with a small telemetry load.

Those are the five difference modes of storage in the right-hand column -- kind of summarize what we're doing with them.

The simulated eclipse season is not really as neat as one would like it to be in a simulation of a true synchronous orbit application. It consisted of 30 cycles of 1.2 hours at a C over 2 discharge rate and then a recharge for 10.8 hours. So we were running a 12-hour cycle; it was semi-accelerated, 30 cycles worth, every 120 days.

And, as I emphasized, this is a real time test. Okay, the next viewgraph, Floyd, please?

(Slide 42.)

Prior to each simulated eclipse season and after reconditioning at least on four packs which are reconditioned, the fifth one was not, actually Pack No. 3. We would run capacity tests.

Here, for instance, in this five-cell battery pack, are the capacities as a function -- it says test number, it's actually the function of each simulated eclipse season -- the eighth season is four years of real time.

The temperature is between 60 and 70 degrees Fahrenheit throughout the four years. As you can see, Pack No. 3, which is on continuous trickle-charge with no reconditioning prior to the start of the 30 cycle eclipse season, has been showing an increased capacity year by year to an essentially 1.15 volt per cell average, which indicates perhaps a sharpening of the knee of the curve -- at least for that particular pack.

As you can see the pack with the highest capacity is No. 5. That was open circuit discharged with the telemetry load. Pack No. 4 is continuously trickle-charged at C over 36 with reconditioning.

Pack No. 2 is open circuit charged stand with cycling every 30 days to recondition it and Pack No. 1 is simply charged every 30 days in a top-off manner and that one -- at least in that capacity with those measurements -- does not look nearly as good as the others.

The next viewgraph, I believe, will show the capacities to 5.5 volts for the pack, which is a little bit lower in the discharge curve to roughly 1.1 volts per cell.

(Slide 43.)

The order hasn't changed. The open circuit discharged pack looks the best. The pack which is simply top-off charged every 30 days looks the worst. And, again, Pack No. 3 has shown increasing capacity season by season.

Next one, please?

(Slide 44.)

And now the capacity to 5 volts, which is a standard to which a lot of people measure cells, shows interesting -- Pack No. 5, of course, still looks quite good -- we do see capacity growth with time, presumably perhaps corrosion of the positive electrode sinter.

CAP TEST TO 5.75 V

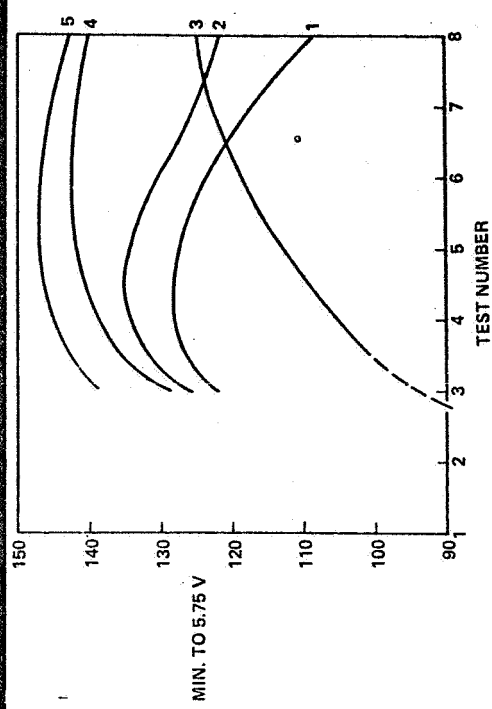


FIGURE 42

36368-9

TEST
CONDITIONS

PACK NO	CONDITION	PRECONDITION STORAGE / POOL
1	LOAD CHARGE RECONDITIONING	OPEN CIRCUIT WITH PERIODIC TOP OFF CHARGE
2	LOAD CHARGE	OPEN CIRCUIT WITH PERIODIC RECONDITIONING
3	RECONDITIONING	
4	LOAD CHARGE RECONDITIONING	
5	LOAD CHARGE RECONDITIONING	

*LOAD OF 100 mA DURING 1ST AND 2ND SESSIONS

RECONDITIONING PROBLEMS
STEP 1: 100 mA FOR 12 HRS
STEP 2: 100 mA FOR 12 HRS
STEP 3: 100 mA FOR 12 HRS
STEP 4: 100 mA FOR 12 HRS
STEP 5: 100 mA FOR 12 HRS

36368-1

FIGURE 41

CAP TEST TO 5.5 V

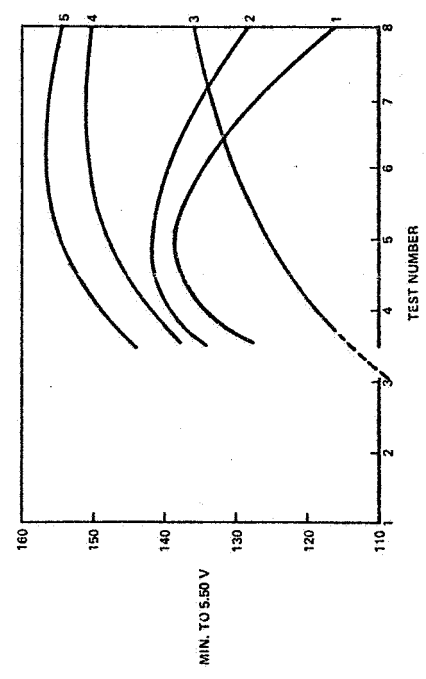


FIGURE 43

36368-13

CAP TEST TO 5.0 V

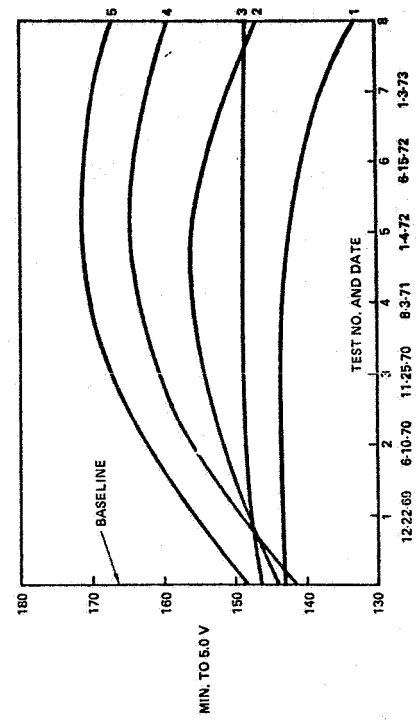


FIGURE 44

36368-13

73a

Pack No. 5 still looks the best, as you can see, from 1969 all the way to 1973. Season No. 8 is in September of 1973, it's just completed. And Pack No. 4, again, still looks second-best in capacity.

And interesting that the capacity to one volt per cell for Pack No. 3 has really not changed since the test started, whereas, as you saw before, it was increasing to 1.15 volts and 1.1 volts, which indicates a sharpening in the knee of the curve and I don't yet understand exactly why it's doing that. I invite comments later on.

Pack No. 2, which is cycled every 30 days, reconditioned every 30 days, does not look as good as 4 and 5, of course. And No. 1 still looks the worst in terms of capacity and that was simply charged every 30 days during the non-eclipse period.

Next one, Floyd, please?

(Slide 45.)

Here's the end of discharge voltage for each pack in the first simulated, 30-cycle eclipse season. As you can see, they're pretty well grouped. Pack No. 5 generally started off the test looking a little bit better than the others and Pack No. 1 was the lowest of them.

The other three were pretty well grouped together. It shows in that first season what would normally be expected -- a low decline in the discharge voltage.

(Slide 45a.)

The next viewgraph shows the -- after two years in the fourth season, 1971 -- this one has some end-of-charge data also plotted on the upper part of the graph for the last half of the test and, as you can see, by the fourth season we have considerably more divergence in the end-of-discharge voltage characteristics of each pack.

But Pack No. 5 is still right up there. However, Pack No. 1 has come up considerably from last place to second place. They're still reasonably well grouped together. I don't see anything that really separates after two years one method from the other in terms of end-of-discharge voltage through any simulated eclipse season.

However, looking at the end-of-charge voltage, we do see a significant difference and Packs 3 and 4, the two packs which are on continuous trickle charge for the non-eclipse

period, are showing significantly lower and perhaps more uniform end-of-charge voltages, cycle-by-cycle, after two years. The end-of-charge voltages for packs 1, 5 and 2 are considerably high.

Now, the next viewgraph shows the same kind of data. We had a little test problem there on Pack 5, as you can see. I don't think the battery exhibited that kind of behavior. This is the seventh simulated eclipse season and we still in the end-of-discharge voltages see further spreading of the characteristics over the eclipse season cycle-by-cycle.

(Slide 46.)

Pack 5 still looks great and that's the one that's stored open circuit discharged with a small telemetry load on it. The end-of-discharge voltage has shown less deterioration than the others.

Pack 1 and 2 are still not too bad, although Pack 4 is looking almost as good as Pack 5 and that's the one that's continuously trickle-charged and reconditioned before each eclipse season.

Next viewgraph, please?

(Slide 47.)

Left a viewgraph out, it may be a little hard to see. On the left-hand side, we plotted the end-of-discharge voltage for each pack on the bottom of the left and the end-of-charge voltage for each pack on the upper left for the early part of each eclipse season, year by year, during the first four or five cycles.

We picked a point, I believe, at about the third or fourth cycle of each season and then plotted the end-of-charge voltage year by year and the end-of-discharge voltage year by year.

Pack No. 5 clearly -- this data is slightly smooth from some of that test data you saw -- but Pack No. 5 in the early cycles of each eclipse season each year immediately or rather began to show a trend toward high end-of-charge voltage, whereas the other packs, especially Pack 4, which is the continuous trickle-charge with reconditioning, Pack 4 showed steadily decreasing end-of-charge voltages year by year.

If you looked at the early performance in each eclipse season, however, in conjunction with the increasing

FIRST 30 CYCLE SIMULATED ECLIPSE (1-70)

HUGHES
AIRCRAFT COMPANY

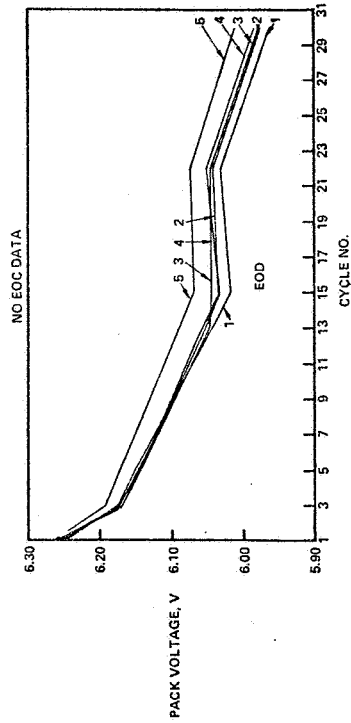


FIGURE 45

FOURTH 30 CYCLE SIMULATED ECLIPSE (8-4-71)

HUGHES
AIRCRAFT COMPANY

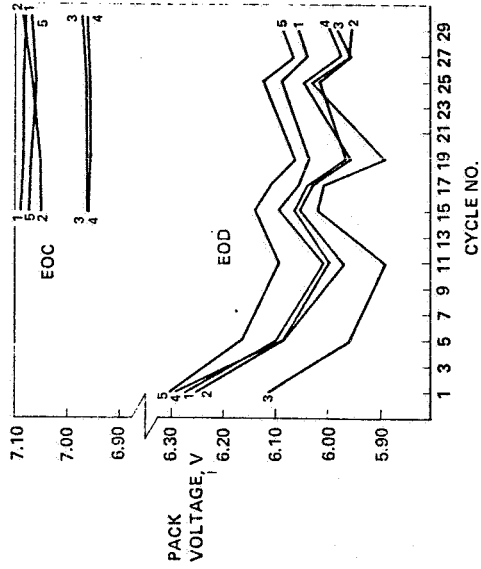


FIGURE 45A

36368-6

SEVENTH 30 CYCLE SIMULATED ECLIPSE (1-4-73)

HUGHES
AIRCRAFT COMPANY

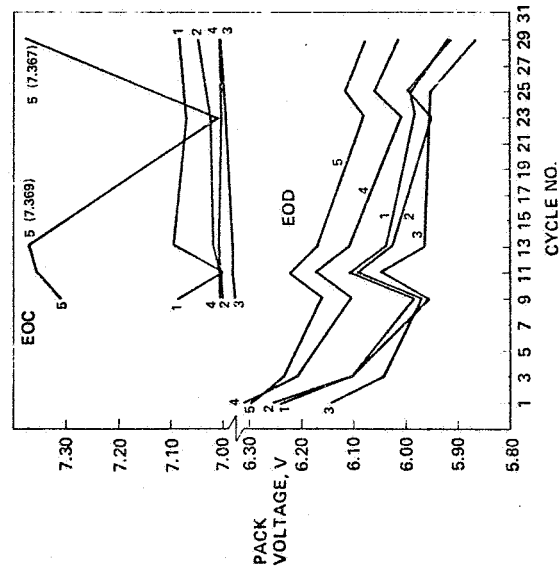


FIGURE 46

36368-7

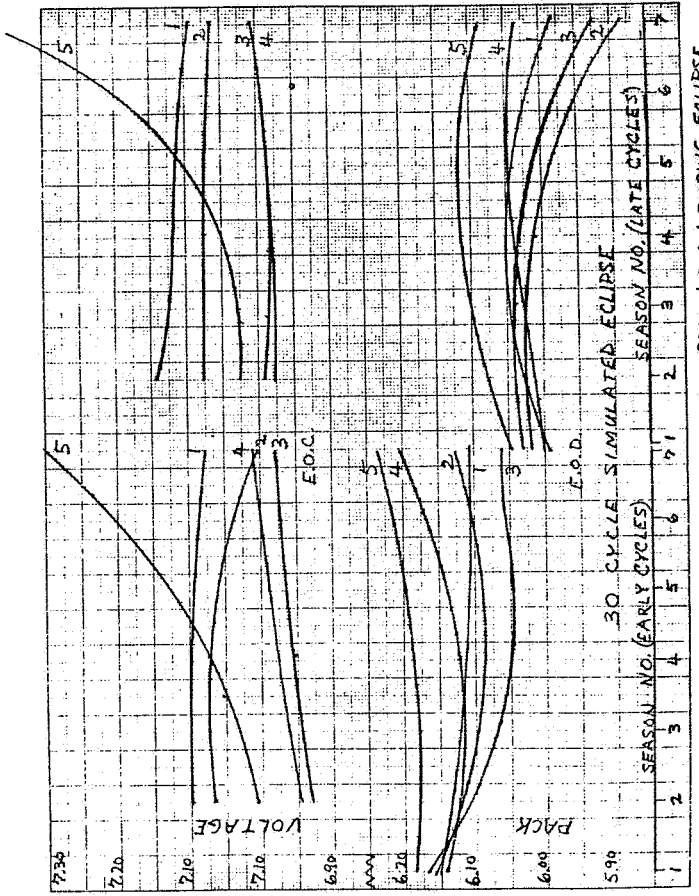


FIGURE 18. SMOOTHED DATA, EOCV & EODV DURING ECLIPSE

FIGURE 47

75a

end-of-charge for Pack No. 5 year by year, it also exhibited end-of-discharge voltages which were improving season by season, looking at the same cycle in each year, as did Pack No. 4.

Packs No. 1, 2 and 3 were fairly uniform for the four years and did not degrade significantly early in the eclipse season. Looking at the 30th cycle in each eclipse season year by year we still see that Pack No. 5 is showing significant increase in end-of-charge voltage.

I don't see any kind of self-reconditioning or anything like that late into each eclipse season. I see no change in the end-of-charge voltage. The trend is still toward a very rapid rise and by the end of the eighth season, the test on Pack 5 was terminated due to severe bulging and obvious gassing in the cell, which one would expect at the voltage that it did get to.

Packs 3 and 4, the two packs that are trickle-charged, again show the lowest and most consistent end-of-charge voltages over the four years late in the eclipse season. As far as end-of-discharge voltage is concerned, Pack 5 still showed the best end-of-discharge voltage and I'm conjecturing that we don't see an electrolyte redistribution problem.

I would expect to see low end-of-discharge voltage for that pack, if it were dry, for instance, and we don't. The discharge voltage performance is excellent in Pack No. 5 even though the cells were swelling and we had to terminate the test.

And, again, Pack 4 clearly stands out over the four-year period as providing the most uniform end-of-discharge voltage characteristics, whereas Packs 1 and 3 and 2 are a little lower and degrading can be seen with time.

Okay, next one, please, Floyd?

(Slide 48.)

This is kind of a busy-looking thing. I won't dwell on it. Perhaps we can look down toward the bottom. This shows a summary, cell by cell of each pack in the end-of-charge and end-of-discharge voltages, every season.

And looking down, this is for the 30th cycle in each season. Looking down at season No. 8 at the bottom and reading across for the end-of-charge and end-of-discharge voltages for each pack.

Note that Pack 5, as I said which we did terminate, showed the highest and most uniform end-of-discharge voltage performance of any of the packs. It was really excellent. It just varied cell by cell, just by millivolts after four years.

However, the end-of-charge voltages, as you can see, are all low -- all except one -- the center one is very low, it's a gauge cell and it's leaking. And I tend to discount that kind of performance.

The other four cells all are well above 1.5 volts and obviously contributed -- was the cause of the swelling or a symptom of the gassing. The Pack 1, which is just top-off charged periodically, is not too bad, showing low charge voltages, a reasonably good end-of-discharge voltage.

Pack 2, likewise, Pack 3, also shows relatively uniform end-of-discharge voltages for this 1.2 hours cycle at C over 2. However, Pack 4 generally seems to produce the next best end-of-discharge voltage from Pack 5 and fairly uniform and low charge voltages.

The next viewgraph summarizes this one, perhaps it's a little clearer.

(Slide 49.)

The maximum voltage difference within each pack is plotted here from the highest cell to the lowest cell for each season. If you run down and look at the voltage divergence, for instance, the end-of-discharge voltage divergence for each pack, you'll note that it approaches a minimum toward the fifth season, invariably, which I find interesting.

It seems that the characteristics of each pack, the individual cells are converging season by season to the fifth season and then they begin to separate and diverge sharply. However, the two packs which generally showed the best composite performance in both end-of-charge and end-of-discharge voltage are Packs 3 and 4, both of which are on continuous trickle-charge, although Packs 2 and 1 are still showing acceptable performance.

Next one, please, Floyd?

(Slide 50.)

This is kind of a summary and it's my own ranking, if one wants to rank the performance over four years as to what the impression gained from the data is for these cells

PACK CELL VOLTAGE DIFFERENCE VS SEASON DURING ECLIPSE SEASON (LATE CYCLES)

SESSION NO.	MAX VOLTAGE DIFFERENCE WITHIN EACH PACK, MV											
	PACK 1		PACK 2		PACK 3		PACK 4		PACK 5			
	EOC	EOD	EOC	EOD	EOC	EOD	EOC	EOD	EOC	EOD		
1	-	20.6	-	24	-	11.7	-	16.8	-	18.4		
2	19.9	19.6	13	10.9	13.2	17.8	14.5	18.7	19.6	16.9		
3	23	17	16	12	11	15	13	12	31	26		
4	28	15	18	14	17	17	19	32	12			
5	39	11	20	7	6	2	9	5	31	6		
6	25	22	17	14	10	12	17	14	45	5		
7	30	73	9	31	12	28	20	19	94	7		
8	32	46	43	65	13	32	35	24	130*	7		

FIGURE 49

INDIVIDUAL
CELL VOLTAGES
ECLIPSE SEASON,
LATE CYCLE NO.

NOBY35	PACK 1			PACK 2			PACK 3			PACK 4			PACK 5		
	EOC	EOC	EOC	EOC	EOC	EOC	EOC	EOC	EOC	EOC	EOC	EOC	EOC	EOC	
1	1.0313	1.0941	1.4248	1.1955	1.4061	1.1948	1.4063	1.1920	1.4190	1.1719	1.4093	1.1921	1.4038	1.1719	
2	1.4213	1.1941	1.4245	1.1950	1.3932	1.1737	1.3969	1.1735	1.3993	1.1656	1.3969	1.1737	1.4038	1.1719	
3	1.4207	1.2002	1.4135	1.1891	1.4034	1.1891	1.4034	1.1891	1.4034	1.1891	1.4034	1.1891	1.4034	1.1891	
4	1.4263	1.1648	1.4135	1.1962	1.1953	1.1953	1.1953	1.1953	1.1953	1.1953	1.1953	1.1953	1.1953	1.1953	
5	1.4406	1.2039	1.4235	1.1990	1.4114	1.1935	1.4114	1.1935	1.4150	1.4082	1.4114	1.1935	1.4150	1.4082	
6	1.4273	1.2228	1.4111	1.2222	1.4004	1.2222	1.4004	1.2219	1.428	1.221	1.4004	1.2219	1.428	1.221	
7	1.4422	1.214	1.4111	1.224	1.4057	1.224	1.4057	1.224	1.4057	1.224	1.4057	1.224	1.4057	1.224	
8	1.4422	1.214	1.4111	1.224	1.4057	1.224	1.4057	1.224	1.4057	1.224	1.4057	1.224	1.4057	1.224	
9	1.4422	1.214	1.4111	1.224	1.4057	1.224	1.4057	1.224	1.4057	1.224	1.4057	1.224	1.4057	1.224	
10	1.4422	1.214	1.4111	1.224	1.4057	1.224	1.4057	1.224	1.4057	1.224	1.4057	1.224	1.4057	1.224	
11	1.4422	1.214	1.4111	1.224	1.4057	1.224	1.4057	1.224	1.4057	1.224	1.4057	1.224	1.4057	1.224	
12	1.4422	1.214	1.4111	1.224	1.4057	1.224	1.4057	1.224	1.4057	1.224	1.4057	1.224	1.4057	1.224	
13	1.4422	1.214	1.4111	1.224	1.4057	1.224	1.4057	1.224	1.4057	1.224	1.4057	1.224	1.4057	1.224	
14	1.4422	1.214	1.4111	1.224	1.4057	1.224	1.4057	1.224	1.4057	1.224	1.4057	1.224	1.4057	1.224	
15	1.4430	1.221	1.412	1.222	1.409	1.229	1.409	1.229	1.438	1.243	1.409	1.229	1.438	1.243	
16	1.424	1.226	1.438	1.236	1.403	1.227	1.403	1.228	1.415	1.237	1.403	1.228	1.415	1.237	
17	1.424	1.226	1.438	1.236	1.403	1.227	1.403	1.228	1.415	1.237	1.403	1.228	1.415	1.237	
18	1.414	1.235	1.406	1.229	1.404	1.227	1.402	1.228	1.418	1.242	1.402	1.228	1.418	1.242	
19	1.453	1.235	1.416	1.235	1.409	1.232	1.408	1.232	1.458	1.243	1.408	1.232	1.458	1.243	
20	1.423	1.211	1.399	1.200	1.411	1.209	1.405	1.216	1.467	1.222	1.405	1.216	1.467	1.222	
21	1.415	1.210	1.404	1.213	1.393	1.203	1.393	1.203	1.429	1.210	1.393	1.203	1.429	1.210	
22	1.450	1.191	1.414	1.259	1.391	1.199	1.391	1.205	1.420	1.222	1.420	1.205	1.420	1.222	
23	1.413	1.213	1.403	1.207	1.401	1.207	1.408	1.213	1.423	1.223	1.408	1.213	1.423	1.223	
24	1.422	1.202	1.401	1.201	1.019	1.109	1.411	1.213	1.523	1.216	1.411	1.213	1.523	1.216	
25	1.422	1.202	1.400	1.203	1.390	1.213	1.392	1.190	1.429	1.210	1.392	1.190	1.429	1.210	
26	1.396	1.128	1.400	1.203	1.392	1.179	1.392	1.166	1.429	1.210	1.392	1.166	1.429	1.210	
27	1.422	1.202	1.400	1.184	1.404	1.192	1.404	1.205	1.439	1.219	1.404	1.205	1.439	1.219	
28	1.401	1.193	1.404	1.184	1.404	1.192	1.404	1.205	1.439	1.219	1.404	1.205	1.439	1.219	
29	1.418	1.205	1.401	1.207	1.413	1.214	1.403	1.221	1.554	1.235	1.403	1.221	1.554	1.235	
30	1.427	1.205	1.401	1.207	1.413	1.214	1.403	1.221	1.554	1.235	1.403	1.221	1.554	1.235	
31	1.427	1.205	1.401	1.207	1.413	1.214	1.403	1.221	1.554	1.235	1.403	1.221	1.554	1.235	
32	1.427	1.205	1.401	1.207	1.413	1.214	1.403	1.221	1.554	1.235	1.403	1.221	1.554	1.235	
33	1.427	1.205	1.401	1.207	1.413	1.214	1.403	1.221	1.554	1.235	1.403	1.221	1.554	1.235	
34	1.427	1.205	1.401	1.207	1.413	1.214	1.403	1.221	1.554	1.235	1.403	1.221	1.554	1.235	
35	1.427	1.205	1.401	1.207	1.413	1.214	1.403	1.221	1.554	1.235	1.403	1.221	1.554	1.235	

FIGURE 48

OVERALL BATTERY PACK PERFORMANCE AND RANKING

PACK NO	PREF. TO "A", "B" OR "C" WOULD BE CHANGED TO	PERFORMANCE CHARACTERISTICS IN SERVICE	TEST RESULTS			
			100% CAPACITY	100% CAPACITY	100% CAPACITY	100% CAPACITY
1	OPEN, LOCKED, CHANGED TO STAND WITH PLATE ON TOP OFF	STABLE BODY THROUGHOUT TEST ECCN IN CAPACITY TESTS SHOWS TYPICAL TEST DATA	4	3	4	4
2	OPEN DIRECTLY THROUGHOUT TEST AND WITH OPEN LOCK THROUGHOUT TESTING PLATE LOCKING	STABLE BODY THROUGHOUT TEST OPEN LOCK TEST WITH PLATE THROUGHOUT TEST	4	3	2	3
3	THICKER CHARGE AT 360 CONTINUOUSLY THROUGHOUT	STABLE BODY THROUGHOUT TEST OPEN LOCK TEST WITH PLATE THROUGHOUT TEST	3	4	1	1
4	THICKER CHARGE AT 360 CONTINUOUSLY THROUGHOUT PLATE LOCKING	STABLE BODY THROUGHOUT TEST OPEN LOCK TEST WITH PLATE THROUGHOUT TEST	2	2	1	1
5	OPEN, LOCKED, CHANGED TO STAND WITH PLATE ON TOP OFF	HIGHLY CAPACITY AND EOOD THROUGHOUT TEST SLIGHTLY POORER LOCKING AND THROUGHOUT TEST DISCREPANT / BY HIGH LEVELS	1	1	0	0

FIGURE 50

under these circumstances. Pack No. 1, which is periodically charged every 30 days in the non-eclipse season, showed a fairly stable end-of-discharge voltage throughout the test. However, after three years, the capacity began to degrade fairly sharply and in general I think that's probably about the fourth best way of handling these cells under these test conditions.

Pack No. 2 -- all of this is an oversimplification, so bear that in mind -- Pack No. 2 is open circuit charged stand, with periodic cycling. It's a charge, a discharge and a re-charge every 30 days.

And, again, the end-of-discharge voltage was fairly stable throughout the test, just degraded slowly. The first two years, it looked very good, but then the degradation and the end-of-discharge voltage characteristics, accelerated faster than packs 3 and 4, and this is perhaps consistent with some other data that Jim Dunlop may have gotten at Comsat also.

Pack No. 3, which is trickle-charge continuously, has no reconditioning before each eclipse season, nor reconditioning before each capacity measurement prior to the eclipse season, showed a steadily increasing end-of-discharge voltage eclipse season by eclipse season at least in its characteristics to 1.15 volts and 1.1 volts and remained pretty stable in capacity to a volt throughout the test.

The end-of-charge performance was very uniform and very little difference between typical end-of-charge voltages from the first season to the eighth season. Pack No. 4, which is continuously trickle-charged at C over 36, was reconditioned before each eclipse season and that one, I think, based on the data I've seen, generally showed the most stable and uniform performance over the entire four years -- a very acceptable end-of-charge voltages and very acceptable and uniform end-of-discharge voltages over all eight seasons.

The fifth pack to the time we terminated the test had very good end-of-discharge voltage performance and very good capacity. However, it had extremely high end-of-charge voltages after four years and it was just steadily rising the whole four years.

It's not truly open circuit discharged. It does have this small, 322 microamp. telemetry load on it and what the effect is, I cannot be certain. None of these cells have been opened up and analyzed as yet. I believe some of the cells in Pack 5 are probably being opened and going through analysis this week.

And we intend to do a full chemical and electrochemical measurements on the cells and therefore, since we haven't really done any good analysis, but we intend to sample the others that are still running shortly. I won't conjecture on what's providing us with this kind of performance, but rather just present you with the data and let you draw your own conclusions.

I think that's all I have and I'm open for questions.

FORD: Joel Bacher, RCA?

BACHER: I have several questions. Could you describe the reconditioning process?

KRAUSE: The reconditioning process primarily consisted of a charge first of approximately C over 20, in that neighborhood and then a discharge around C over 60 to 1.1 volt per cell average, a low rate deep discharge, and then a recharge at about C over 12. It was just a single cycle.

BACHER: Did you consider storing the cells in individually shorted conditions?

KRAUSE: No, that was not considered for purposes of this test, primarily because, as I say, the test started out as application to gain information for a particular system and it wasn't deemed practical at that time, nor is it normally the case that this kind of spacecraft to store cells shorted.

The battery does have to be available to support the spacecraft even in the sun periods.

BACHER: Okay, one last question. Could you repeat your description of the cycle during the 30-day cycle?

KRAUSE: Yes, it was a 1.2 hour discharge at C over 2 and a 10.8 hour charge at C over 10. That's about 160 percent recharge fraction. Again, it's not a real good simulation of a true synchronous eclipse.

BACHER: It is a definite discharge? What is the depth of discharge.

KRAUSE: It was approximately 60 percent depth of discharge, a 15 amp/hour cell.

BACHER: Thank you.

HELLER: If you took Pack 1 and converted it to cycle four, what do you think would happen?

KRAUSE: Pack No. 1? It's a good question. I don't know. I think personally, again, I hate to get trapped into this without having done, say, an electrochemical measurement on the plates of a cell, which we are going to do shortly.

I have a sneaking suspicion that most of the packs -- well, Packs 1 and 2, primarily -- are probably going to show a fairly low negative capacity and in fact show not only that, show very low and inactive discharge cadmium and I would expect that if we took Packs 1 and 2 and put them onto trickle charge, that we may see some significant swelling.

We will probably have the negatives pretty well charged up before very long. Pack 1, by the way, is showing now -- one or two cells -- showing a slight sign of swelling and to me, at least, under these conditions, mean that we're probably running out of discharge negative.

These cells are a garden variety, 1969, 15 amp/hour cells and have a fairly high pre-charge and you start out with a fairly discharge negative capability.

SULKES:(US Army Electronics Command) One question about your reconditioning cycle -- you use a C over 60 discharge rate is that correct?

KRAUSE: Correct.

SULKES: Is there any reason this was chosen? It seems the data shows that these lower rate discharges tended to grow cadmium crystals.

KRAUSE: You're right. The C over 60 discharge was chosen as many people are aware of who've worked with flight spacecraft, the C over 60 discharge was chosen such that if a relay failed on the spacecraft during reconditioning, the low rate charge capability could supply the demands of the load and essentially bias it out so that it would not discharge the battery, in the event of this relay failure.

It was not really chosen as something which is optimum for the battery, but rather a system consideration. I might point out that on one of our newer spacecraft, really an upgraded, a new version of the Unicef 4.

It'll have a discharge rate for reconditioning around C over 30, which I think is a little more acceptable and it's a compromise. I got some of the systems type guys to compromise and let us do a little something better for the battery, which is, I think, that's in the right direction.

I agree with your comment about the Fritz Ville's paper.

LURIE: (Gulton) Just a comment. On sealed commercial cells we found that when they are stored in a partially discharged state, C over 20 is too rapid a rate. If they are stored for long periods of time in a partially discharged state, C over 20 is too rapid a rate.

You have to go to C over 30 or C over 40.

KRAUSE: Yes, I think there is evidence to show that after long periods of storage, even open circuit discharged or even on charged stand, if -- in our tests, our time exceeded 30 or 40 days and even in just charged stand -- we would have to go to C over 20 or there would be significant hydrogen gassing.

We did not see a problem with these cells at C over 20 even after long period, though. It seems to be low enough.

BOGNER: (JPL) It looks like initially it was quite a spread of capacities over cells, if I read it right.

KRAUSE: Yes, you read it right. These were the five-cell groups. The baseline capacity was slightly different on all of them. I think they range from around 16 amp/hours, $16\frac{1}{2}$ up to around 19, and that did explain some of the spread in the first eclipse season.

It, however, didn't explain the relative, you know, the difference in the change as we went along from season to season.

FORD: Do you have any other questions? Okay, thank you very much. Our next presentation is by Mr. James Dunlop, Comsat Laboratories. The subject is storage experience, (Intercept) for nickel/cadmium cells. Jim?

DUNLOP: Thank you, Floyd. The subject I'm going to talk about today is the storage experience we've had on the (Intercept) for nickel/cadmium cells and in some regard is quite similar to the paper just presented.

First viewgraph, Floyd.

(Slide 51.)

This is a summary of cells that we analyzed that had been stored. We analyzed in this year of 1973. Those

cells had been stored for approximately three years in the various modes shown in this table. The four cells that were received from Hughes Aircraft, the Lot 1 cells had been stored shorted, the Lot 2 cells open, and for comparison we took two cells that we had from Lot 6 that had been stored open and one cell we used as a baseline.

Now, these cells that were stored open were discharged and then stored open. Next slide, please?

(Slide 52.)

The cyclic testing that was done on these cells prior to the analysis is as follows: we reconditioned these cells at 20 degrees C, charging at a C over 20 rate for 48 hours, discharged to one volt at a C over 2 rate, charged at a C over 10 rate for 17 hours and discharged again to 1/10 of a volt at a C over 2 rate.

We then performed a charge retention test, which was a C over 10 charge for five minutes and the voltage measured then and after 25 hours of spin and then we performed this low temperature overcharge test. It was charged for 66 hours at a C over 20 rate and then a discharge at a C over 2 rate to one volt.

The one Comsat cell, the serial number 1056, was opened immediately with no testing just to see if there was any effect due to the cycling. Next viewgraph.

(Slide 53.)

This basically shows the cell performance on the reconditioning, the low temperature and the charge retention. The voltage appear okay here at the -- this is the end-of-charge voltage at the C over 20 rate -- this is the ampere hour capacity measured to 1/10 of a volt.

These are fifteen ampere hour cells ready. You notice they have really about 22 ampere hours capacity. Now, if you actually made that same test probably initially you would have gotten about 1 ampere hour less in capacity.

In general, they have a tendency to increase by about 1 ampere hour or more in the two years. The second reconditioning shows basically, again, acceptable voltages at the end-of-charge and roughly the same capacity when discharged at a C over two rate to a 1/10 of a volt.

The low temperature test didn't really show anything conclusive. But interesting enough, you will note that

on the Lot 2 cells, the voltage on these particular cells was quite a bit higher than on the Lot 1 cells or on the Lot 6 cells. And it turns out later that these cells do have a very little charge, if any overcharge protection.

So, while the test isn't very clear, it gives some indication here at this point in time of a problem that showed up later, which was the fact that the cells have very little overcharge protection.

Again, the capacity measurements look good and the charge retention of all other cells passed the charge retention. Next viewgraph, please?

(Slide 54.)

This is the electrolyte analysis. For the Lot 1 cells, the total weight of the electrolyte was 74 grams, 16.8 grams of KOH and 7 grams of potassium carbonate. On a percent basis, this is about 10 percent potassium carbonate. If you convert that back to KOH, you determine that you should have had about 31 percent KOH in the electrolyte originally.

For the Lot 2 and the Lot 6 cells, first of all, you'll notice that there's a significant different in the amount of electrolyte total. I think this was a change that occurred. The Lot 1 cells are really engineering cells and I think they went through a number of perturbations.

Suffice to say, that's about 20 percent more electrolyte than we've normally observed in any other of the other lots that we've analyzed. But it does point out something else -- when you do run the test, you've got to be a little bit careful because there certainly are variations between lots.

Again, the carbonate level here that we did observe, is about 11 percent, 11 percent to 12 percent, for the Lot 2 and the Lot 6 cells. In our baseline cell it was about 9 percent and 9 percent is more typical for what we see when we do an analysis on this cell very early in it's life.

So, the fact that these cells were stored inactive, nevertheless, we are observing that the storage cells do have an increase of between 1.5 and 2 grams of potassium carbonate as compared to our baseline cells, which were predominantly Lot 6 cells that we analyzed in 1969.

Next graph, please?

(Slide 54a.)

Summary of Cells Analyzed

Source	S/N	Lot	How Stored
H.A.C.	76	1	Shorted since 1-70
	82	1	Shorted since 1-70
	10	2	Open since 12-70
	12	2	Open since 12-70
COMSAT Lab	105	6	Open since 2-70
	149	6	Open since 2-70
	147*	6	Base-line, no storage

* The base-line cell is representative of the lot 6 cells as initially received at COMSAT Labs.

FIGURE 51

Table 1 Cell Performance

S/N	1st Rec.		2nd Rec.		Low Temp.		Charge Ret.	
	C/20		C/10		C/20		Voltage	
	EOCV	Capacity to 0.1V	EOCV	Capacity to 0.1V	EOCV	Capacity to 0.1V	1 hr	25 hr
76-01	1.456	22.25	1.461	22.00	1.495	21.00	1.225	1.211
82-01	1.458	21.87	1.463	21.75	1.493	20.37	1.228	1.214
10-02	1.473	22.00	1.474	21.62	1.543	22.00	1.200	1.184
12-02	1.476	21.87	1.480	21.37	1.548	21.67	1.205	1.186
105-06	No electrical testing		23.00					
149-06	1.470	22.37	1.479					
147-06	1.436	21.12	1.420	21.20	1.474	21.12		

All discharges at C/2.
C = 15A-Hr.

Cells stored open circuited have higher end of charge voltages (EOCV).

FIGURE 53

Cycle Testing

The cells received from HAC were:

Reconditioned 20°C

- Charged at C/20 rate for 48 hours
- Discharged to 0.1 volts at C/2 rate
- Charged at C/10 rate for 17.5 hours
- Discharged to 0.1 volts at C/2 rate.

Charge Retention 20°C

- Charged for C/10 for 5 minutes
- Voltage measured on stand after 25 hours.

Low Temperature Test 0°C

- Charge for 66.5 hours at C/20 rate
- Discharge at C/2 rate to 0.1 volts.

One COMSAT cell S/N 105-06 was opened immediately with no electrical testing. The other cell was cycled for fifteen twelve-hour cycles before chemical analysis.

FIGURE 52

Table 2 Electrolyte Analysis

S/N	Electro-lyte Wt in g	KOH Wt in g	KOH %	K ₂ CO ₃ Wt in g	K ₂ CO ₃ %	Original KOH %
76-01	74.6	16.8	22.6	7.74	10.4	31.6
82-01	73.9	16.8	22.8	7.57	10.3	31.8
10-2	63.5	15.3	24.0	7.46	11.8	34.0
12-2	62.6	15.0	24.0	7.19	11.5	34.0
105-6	59.0	13.7	23.2	7.20	12.2	33.9
149-6	62.6	13.9	22.2	6.91	11.0	31.9
147-6	59.3	14.6	24.7	5.54	9.4	32.9

• Lot 1 cells have twenty percent more electrolyte than lots 2 and 6.

• All stored cells have 1.5 to 2.0 grams more K₂CO₃ than base-line cell regardless of storage mode or subsequent operation (i.e., S/N 105-06).

FIGURE 54

83a

This shows a breakdown of the component weights. The Lot 1 cells -- I don't understand this -- they did have slightly lighter weight electrodes. I didn't know what to attribute that to. Probably the most significant thing here, again, is that we are observing relatively significant variations in weight on the negative electrodes.

Variations can be as much as 10 to 20 percent. Next viewgraph, please?

(Slide 55.)

This shows the electrochemical and chemical analysis for these cells. Probably the most significant thing to point out is that in the Lot 2 cells, there is an excessive amount of total precharge, 17 to 18 ampere hours of precharge.

That's total precharge -- that's the amount that you determine chemically and electrochemically. The actual total cadmium chemically determined in this particular plate is about 46 ampere hours and this is a 15 ampere hour cell.

This is typical of a nickel/cad design, certainly in 1969. But a typical number for the total precharge for our baseline cell was about 12 ampere hours to about 14 ampere hours. So this number here is quite large and does account for the fact that we were very marginal and had practically no overcharge protection in these Lot 2 cells.

Next viewgraph.

(Slide 56.)

This shows a bar graph of the cadmium electrodes. The bar graph that we have really shows the state of charge of the cadmium with regards to the positive electrode. The bottom portion here represents the unusable precharge -- that's the amount of cadmium that's remaining in the electrode when you complete discharge it electrochemically.

The portion that you see in here is the usable precharge -- that's the amount that you can electrochemically measure. And this portion here represents the positive capacity -- this is the state of charge -- this is the positive capacity when it's completely discharged, the positive when it's completely charged.

And this portion up there, then, represents the overcharge protection. And, as I say, in these two cells,

there's practically no overcharge protection.

That's all I have to say on the storage modes. I think the point here that I would like to say in summary, is that the variations that we observed between the different watts here and the different storage modes -- certainly the variations were not due to any variations that we could attribute to the storage mode.

The variations that we see here that I've described really seem to be variations that were in the cells initially and while there was some increase in the carbonate level with time, that's the only change that we saw.

And, frankly, we saw very little cadmium migration into the separator. We had no problem removing the separator from the cadmium electrode for these cells regardless of whether we had them standing open circuit or shorted. So, in essence, we didn't really determine about the degradation mechanisms that were occurring for the storage mode were excessive for these particular cells.

Now, I'd like to go on now and describe some work that we have on a real time test similar to the work that was described in the previous paper.

Next one.

(Slide 57.)

This is the -- we have two groups of cells that have been on test for about four years also. There are two different storage modes that we are using. One is a continuous trickle-charge mode during the storage and the other is this open circuit stand with a very low discharge rate and a recharge every 30 days as described previously.

The only difference is that during eclipse season we do not do this. We run a real time eclipse season. That means that we discharge each day in accordance with the depth of discharge we expect to see during eclipse operation and you run the same type of charge mechanisms, which means you charge at, in this case, approximately C over 12 rate until you put in about 15 percent overcharge and you drop back to a trickle charge rate for the remaining 24 hours.

Now, this is a real time simulated eclipse season for this data. Now, what we show here is the results at the end of the seventh eclipse season. We're just showing the data for the 23rd cycle, which is the cycle in the middle.

Table 3 Component Weights (grams)

S/N	Cell Wt.	Neg. Wt. (12 Plates)	Maximum Negative Plate Wt Variation	Pos. Wt. (11 Plates)	Maximum Positive Plate Wt. Variation
76-01	645	235	3.29	188	.89
82-01	642	236	3.29	186	.81
10-02	649	245	2.74	193	.76
12-02	648	247	1.92	192	.42
149-06	645	247	3.74	191	.32
147-06	651	252	1.72	190	.48

- Lot 1 cells have lighter weight electrodes.
- The maximum negative plate weight variation per cell is excessive. Based on average plate weights, the variation is from 10 to 20%.

FIGURE 54A

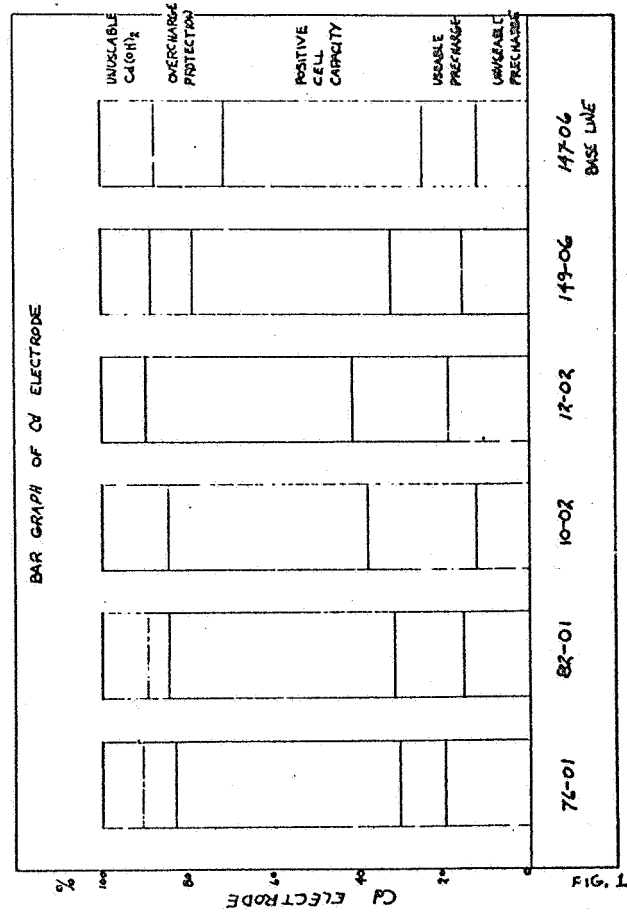


Table 4 Electrochemical and Chemical Analysis

	76-01	82-01	10-02	12-02	149-06	147-06
Electrochemical						
A-Hr Pos. Capacity	21.6	21.7	21.0	21.7	21.9	21.1
A-Hr Elec. Precharge	4.5	6.7	11.5	10.0	6.9	5.7
A-Hr Flooded Neg. Capacity	29.5	30.4	30.7	31.8	34.0	34.2
Chemical						
A-Hr Discharged Cd.	33.2	34.9	39.7	36.4	39.9	39.9
A-Hr Charged Cd	8.1	6.3	5.8	8.6	7.4	6.2
A-Hr Cd Total	41.3	41.2	45.5	45.0	47.3	46.1
A-Hr Precharge Total	12.6	13.0	17.3	18.6	14.3	12.0
A-Hr Overcharge Protection	3.4	2.0	-1.8	0.1	5.2	7.4

- The ampere hour equivalent of total Cd in lot 1 cells is low by about five ampere hours. This is consistent with their lower negative electrode weights. Although the precharge level would normally not be excessive, the lower Cd does not provide for adequate overcharge protection.
- Lot 2 cells have excessive total precharge resulting in no overcharge protection. This condition can not be explained by a shift in state of charge due to storage alone. Calculations based on carbonate level increase and comparison of total precharge levels of lot 6 cells before and after storage would allow for only about a two ampere hour increase. The total precharge in lot 2 cells is excessive by six ampere hours indicating misadjustment at time of manufacture.
- Figure 1 is a bar graph displaying relative state of charge of the above cells.

FIGURE 55

Eclipse Season No. 7

Trickle Storage		Open-Circuited Charged Storage	
Cell S/N	Cycle 7 EOC V.	Cell S/N	Cycle 7 EOC V.
083-06	1.417	096-08	1.413
109-06	1.427	152-06	1.445
124-06	1.425	153-06	1.433
128-06	1.425	076-06	1.413
		097-08	1.408
			1.129

Three cells in the open-circuited charged storage group have EOD V. below the system cutoff voltage per cell of 1.150 V. Cell S/N 096-08 has an EOD V. of 1.050 V. on the 23rd eclipse day. On the 30th eclipse day, a complete discharge @ the c/2 rate was performed on this cell.

FIGURE 57

85a

And for the cells that have been trickle-charged, you'll notice that this is the end-of-charge voltage at the high rate and they do seem to be quite uniform, very much in agreement with the comment that Stan Krause made.

And also you'll notice that the end-of-discharge voltage appears to be rather uniform and not bad. This is about the 23rd day -- that is about a 60 percent depth of discharge.

We actually begin with ten cells and we've periodically done analysis on cells, so we're down to only four cells left and we're fairly careful now about removing these because we want to see how long they really will go.

In the open circuit charged storage mode, we have actually observed two phenomena, as opposed to what Stan mentioned. One phenomena was reported last year and that was a high voltage. We did have one cell that pulled out, developed a high voltage, bulged and was removed from the test.

That cell also had a high voltage at the end-of-discharge. The other phenomena that we are beginning to observe in the last few eclipse seasons -- it started out the sixth eclipse season and it's gotten worse every season so far -- is cells with a low end-of-charge voltage and a low end-of-discharge voltage.

So we're getting both swings in this open circuit stand. We're getting some cells that are going high voltage on charge and high voltage on discharge. We're getting a whole number of different group of cells which is showing up low end-of-discharge voltage and low end-of-charge voltage.

Now, we thought we would explore these particular cells a little bit further. These are all six and a watt six in each cells, by the way. So we took one of these cells and increased the overcharge.

Next viewgraph, please?

(Slide 58.)

This was actually done on the 30th eclipse day and this is the normal discharge only we continued it all the way down now to about 1/10 of a volte and you'll notice that if -- you look at the voltage after about 72 minutes or so, you're getting far down here.

We ran a 60 percent overcharge at the C over 12 rate and we noticed a significant improvement in capacity,

indicating that the problem resulting from the low voltage was actually a charging substance problem, at least indicated by these test results.

We took that cell and put it back in the normal eclipse operation, and the next graph --

(Slide 59.)

-- shows that the voltage started falling right back down again and on the 35th day it was pretty bad, with the normal 15 percent overcharge at the C over 12 rate and then switching the trickle-charge for the remaining time at a C over 36 rate.

And this voltage was beginning to get pretty low here. We went back to a large overcharge and we again observed the same phenomena -- that we had recovered the capacity. The only other data that we have on this particular cell to date is: we thought, "Well, I wonder what will happen if we put it on trickle-charge for a few weeks to see if we covered the charge acceptance?"

And we put it on trickle-charge for three or four weeks and we ran a discharge this week just before the meeting to see if we improved the performance and it turned out we hadn't. We still have this same exact problem with this particular cell, which is that we have a very difficult time charging it.

And, at this point in time, I really don't know why. We haven't done an analysis yet on this cell to try and determine how the -- what's causing the effect that we're observing here.

So, in summary, then, I would like to say that I would definitely agree with Stan that just based on looking at all of the results we have to date on this storage mode, we certainly are getting much more uniform performance and acceptable performance in the trickle-charge mode than we are in this charged open circuit stand with periodic recharge.

Secondly, with this charged open circuit, periodic recharge we are observing two phenomena: one is this high voltage phenomena, which was previously described; the other is -- which has occurred just recently -- is a problem with the charge acceptance of the cell.

Thank you.

FORD: Questions?

87a

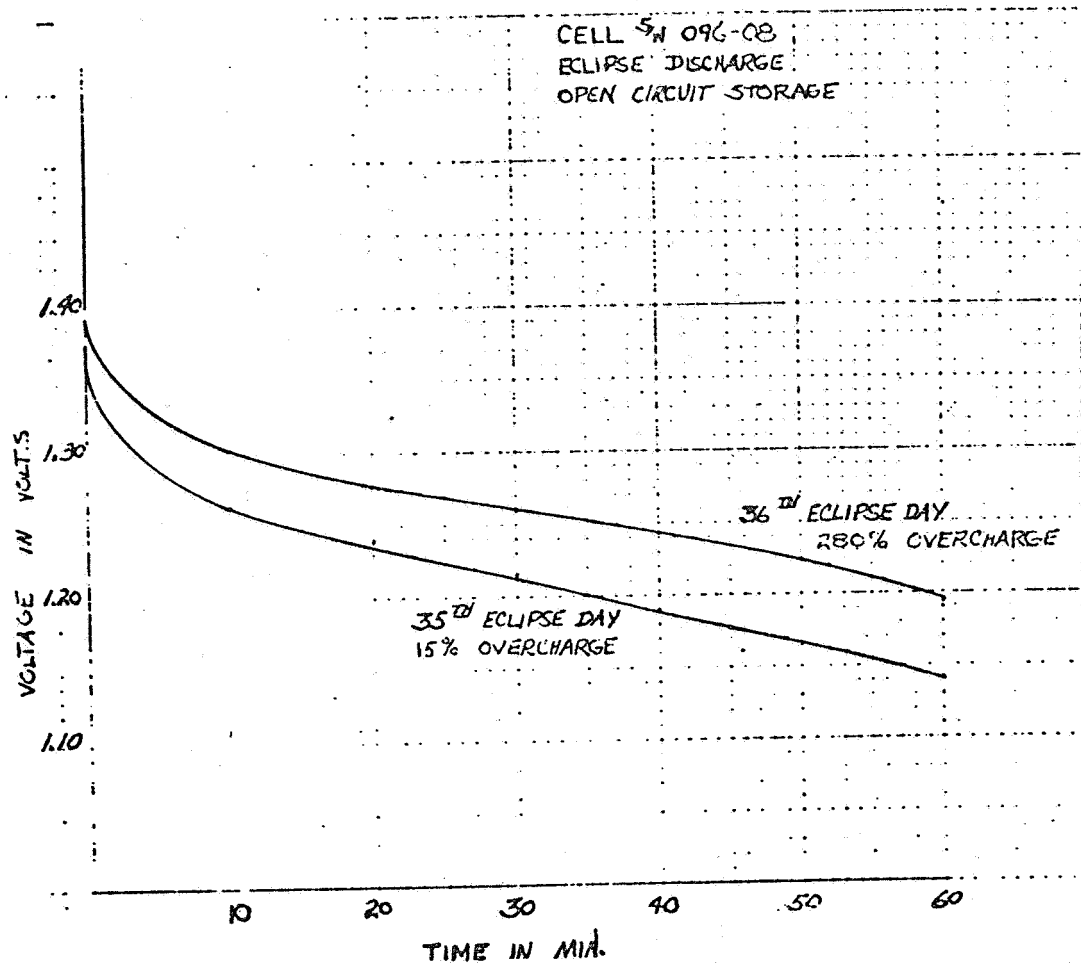


FIGURE 59

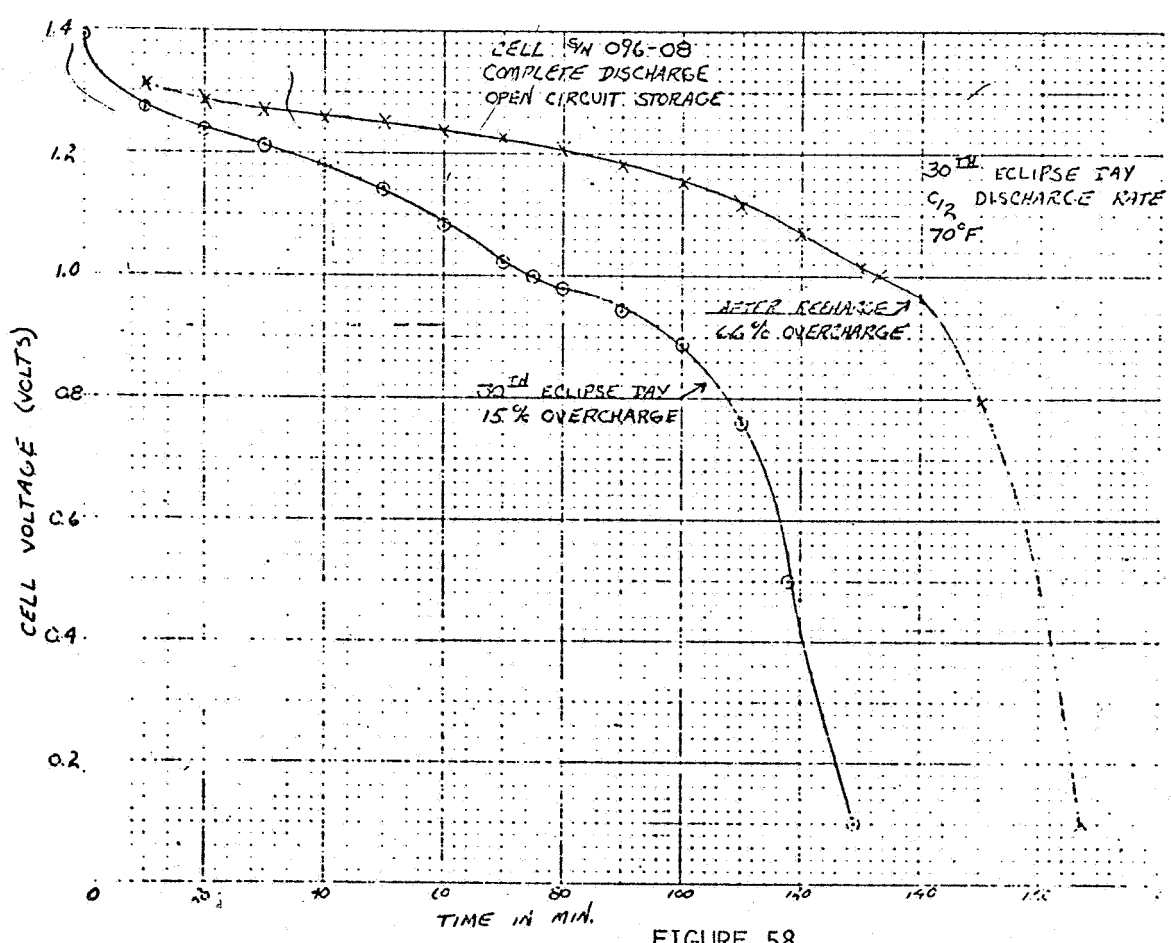


FIGURE 58

STEINHAUER: Jim, do you believe from your last test result that you reported that in going into trickle-charge, that the storage reconditioning mode then has to be selected consistent from the beginning of the mission?

DUNLOP: Well, Bob, you know, you don't want to generalize too much on anything, but certainly all I really said here was that we developed a phenomena that we observed experimentally that occurred after about -- started occurring after about three and a half years of real time testing.

We haven't discovered a way to get out of the problem that's developed.

BOGNER: When you do the overcharge, was that after it was discharged?

DUNLOP: The 166 percent overcharge I showed? That was done immediately after that complete discharge. But, then, you noticed that we put the cell back in the test and continued the normal eclipse operation.

We saw the voltage falling right back off again, so without going through a complete discharge this time, so we'd ignore any reconditioning effect or whatever, we just went to a long overcharge and we got an immediate recovery and we continued in the test and it falls back again. So --

FORD: Other questions?

BACKER: (RCA) You previously reported potential problems with the tenuous trickle-charge, stating a charge to a negative plate. Do you think there might be some compromise trickle value that perhaps is lower?

DUNLOP: Well, let me stated what I previously reported, which was true, and by the way, part of the reason why we chose this storage mode to begin with, I guess. We did observe that when you do continuously trickle-charge, there is this electrochemical oxidation mechanism for forming carbonate and that you do get a greater carbonate build-up with time.

Now, you'll notice that carbonate levels in this cell are pretty high to begin with -- they're like 9 grams or so. The trickle-charge you build up about a gram a year, probably half a gram more per year than you do by the open circuit stand.

And I think this data is pretty well substantiated by the work that Dr. Mallard did at Bell Labs, where he showed the electrochemical, the oxidation mechanism described for his work.

The activation energy was lower for the electrochemical oxidation than for the chemical oxidation. So I think that's probably true, but the results that we're seeing here -- you simply observe what's happening and after four years, the observation is that both for our tests and the work that Hughes has done that you're getting a much better result, so probably the overriding effect is not this carbonate build-up but whatever other mechanisms are running into the picture.

BACKER: Was your trickle rate C over 36?

DUNLOP: Yes, it was.

BACKER: One more thing -- the increased carbonate content, I believe you reported, was related in some way to a loss of overcharge protection.

DUNLOP: Right, well, you can do a direct correlation and if you do that -- it seems that every mechanism that you have reduces the overcharge protection that you conceive. Almost every mechanism that deteriorates performance is at least a reduction in the -- the increase in the positive capacity reduces the overcharge, the oxidation mechanism is about 1.16 or something ampere hour equivalent reduction per gram of carbonate build-up.

BACKER: Okay, my concern is that until you lose all or almost all of your protection, you can't detect what is happening unless you open up a cell.

DUNLOP: Or see the high voltage.

BACKER: Right, that's usually what happens -- you're very near or at the threshold -- so, how do you feel about the fact that the carbonate content is increasing?

DUNLOP: Well, I think probably what I feel is that if you took today's technology, that there's certainly -- you certainly can design with the amount -- there's an excessive amount of precharge in these cells, probably more than you need.

So, probably for say the next generation of cells, we probably would have a higher percent overcharge protection. I think any nickel/cad cell that you build today has a limited

life time and a limited amount of -- another thing that's very important here is -- that is sort of a throw-back to the argumentative days of years ago -- is the whole business of the state of charge adjustment to begin with and the variation that you may run into from lot to lot, for example, or the control of the whole process of the state of charge.

Or you can build a nickel/hydrogen cell -- you're never going to run --

(Laughter.)

UCHIYAMA: Jim, you indicated that you ran a charge retention test on these cells. Was that charge retention just run with the charge just prior to that stand or was it taken from discharge condition?

DUNLOP: No, the charge retention test was on these cells that had been on stand. These cells -- the first group of cells I talked about -- were just on stand for three years. They hadn't been tested. And that was a charge retention test that I showed was simply a charge retention test of cells that have been on stand either shorted or discharged open circuited for three years.

UCHIYAMA: So you discharge it and observed a covering subsequent to that?

DUNLOP: I'm not sure I followed you. I'm not sure I understand the question.

UCHIYAMA: Retention tests can be run a couple of different ways. One is where you just observe the recovery of the discharge, another you infuse a little bit of a charge into it.

DUNLOP: On that particular one we put a C over 10 rate for five minutes or a C over -- I think it was C over 10 for five minutes -- after a complete discharge.

FORD: Steve Gaston, Grumman?

GASTON: (Grumman) One question -- why do you use 25 hours for charging when everybody else uses 24 hours?

(Laughter.)

DUNLOP: I think the guy went home and came back and it was 25 hours instead of 24.

FORD: Questions? In the back?

MIKKELSON: What techniques are you using on INTELSAT 4?

DUNLOP: The actual mode? The worst one. That's right. Unfortunately we're using this particular mode that we've described as probably the worst one.

MIKKELSON: Okay, what's your design objective for your cell on INTELSAT 4, and likewise depth of discharge?

DUNLOP: Seven years.

MIKKELSON: How about depth of discharge?

DUNLOP: Well, it's 60 percent like we were running in the test here.

MIKKELSON: Do you think you'll make it?

DUNLOP: No.

MIKKELSON: How far do you think you'll get?

DUNLOP: I'm not going to answer the question.

FORD: Any more questions?

DUNLOP: Okay, thank you gentlemen.

FORD: Okay, the next subject is by Dr. Will Scott, TRW Systems Group. The title of the subject matter is the effects of open circuit and random use on charged voltage of nickel/cadmium cells. Dr. Scott?

SCOTT: What I'm going to be addressing is the effects of ground storage on subsequent cell charged voltage behavior, so it's a little different than what you've just been hearing, which is related to things practical in orbit.

The first data I'd like to present is nine years old. It relates to effects of storing cells, open circuit, after discharging, as indicated on this first graph, C over two, discharged to one volt, then open circuit.

(Slide 60.)

This graph just depicts the range of behavior of approximately 75 nickel/cadmium cells stored in this mode for

period up to over 60 days. This is the shape of the curve of voltage versus charge time that was used to generate the data that is shown in the next slide.

(Slide 61.)

This is a plot of two things: one, as indicated, the average over 75 cells of the peak maximum voltage observed during a C over 20 charge at approximately room temperature as a function of the time that the cells were stored open circuit after discharging at C over 2 to one volt.

Also plotted here is the standard deviation which indicates another kind of problem that goes right along with the increase in the peak voltage characteristic.

Both of these plots were published in reports, one of them generated under the Orbiting Geophysical Observatory Program -- actually, a report published in 1964.

So the problem is not new and it doesn't appear to have changed much, at least for certain types of cells. We have recently inadvertently run into the same problem.

Now, there's many ways to discharge a cell and this is one thing that tends to lead to confusion and diversion of results. You can discharge it to 1.1, to 1 volt, to 1/10 volt to 0 volts; you can put a resistor on it and you can wait one minute to thousands of minutes and every one of those conditions will give you a different storage behavior. That's aprt of the problem of trying to correlate these different results.

(Slide 62.)

This is basically the same kind of data that I was showing you a few moments ago where this now compares the effects of storage on open circuit after opening the circuit in the fully charged condition versus storing the cell over the same period of time after discharging to one volt.

This plot shows that if anything is worse than storing it open circuit discharge, it's storing it open circuit charged. You might get that general idea from what has been said here before today.

All right, now, recently -- over the last couple of years -- we've encountered a number of situations where batteries have been used for spacecraft testing in the so-called integration or random use mode and then brought back for testing in the laboratory.

(Slide 62a.)

And this is -- a plot of maximum and minimum individual cell voltages in a 22 cell battery versus the battery charge current and temperature along the bottom, down near the bottom of the figure.

In this case, the charge current tapered off because the system was operated with a voltage clamp. When the battery reached that voltage, the current tapered off.

The voltage of the highest voltage cell is increasing very rapidly at that point in time and it's only the fact that the current is dropping off rapidly that keeps the voltage from going much higher than shown on that plot.

This kind of cell voltage behavior in the presence of a tapering current is a danger sign. As a result of this, we took the batter, some of these batteries apart, and charged them in a more controlled fashion.

(Slide 62b.)

The next graph shows the results of charging some typical cells from these batteries compared with a few cells that were purchased at the same time in the same lot, but had

STORAGE EFFECTS

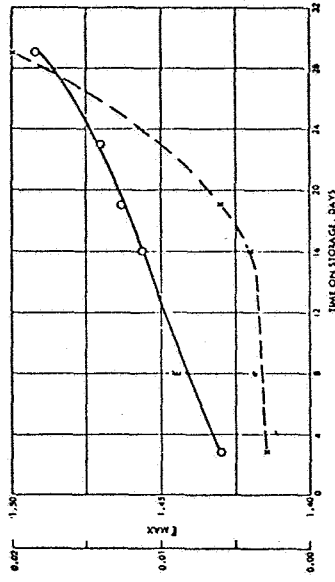


FIGURE 6

AVERAGE MAXIMUM PEAK CHARGE VOLTAGE
AND STANDARD DEVIATION VS. STORAGE TIME
25°C. C/20 CHARGE RATE
AFTER STORAGE OPEN - CIRCUIT, DISCHARGED (C/2 RATE TO IV.)

FIGURE 61

STORAGE EFFECTS

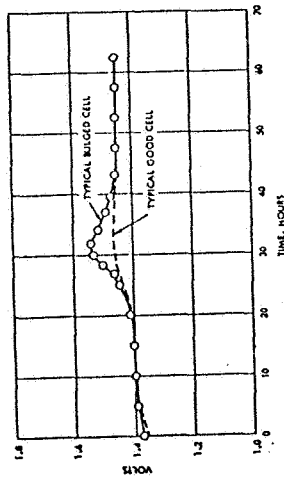


FIGURE 5

CHARGE VOLTAGE CHARACTERISTICS
25°C. C/20 CHARGE RATE
AFTER STORAGE OPEN - CIRCUIT, DISCHARGED (C/2 RATE TO IV.)

FIGURE 60

STORAGE EFFECTS

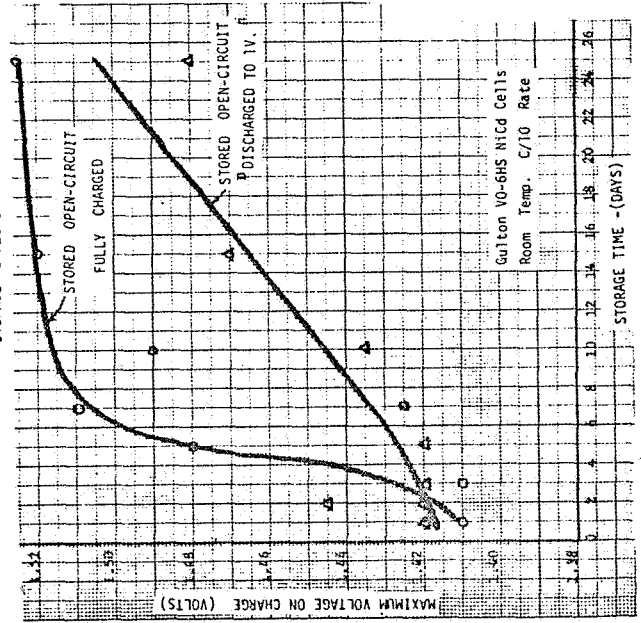
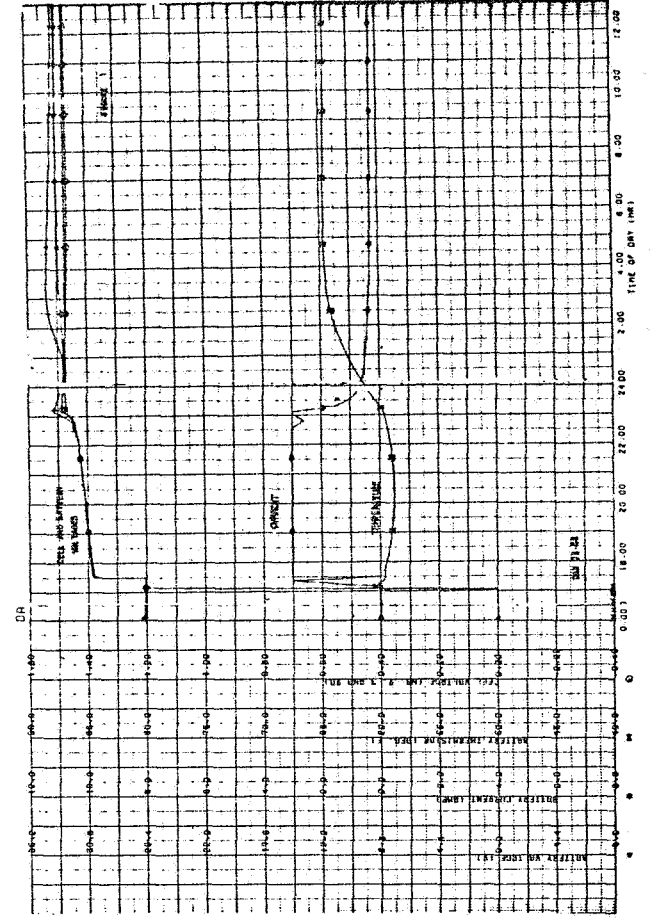


FIGURE 7

MAXIMUM CHARGE VOLTAGE VS. STORAGE TIME

FIGURE 62



Performance data for a 22-cell battery after random
use storage: Constant-current charge with battery
voltage limit (Gulton cells)

FIGURE 62A

93a

not been placed in batteries and had been stored for the same time period.

And this is, as indicated here, a constant current of .6 amp charge. These are nominally 12 ampere hour cells, so this slightly over a C over 20 rate. The temperature you see is 40 degrees Fahrenheit and the cells from the battery -- several of the cells from the battery -- are shown here on this rising characteristic and as labelled here, the cells whose voltages are going along here are the cells that were shorted.

So, in every case the cells from the battery that had been in a random use mode, showed the steeply rising characteristic and in every case the cells that were shorted showed the small rise and then the flat, gradual voltage rise characteristic.

In order to get a bit more information as to what was causing this kind of voltage behavior in the cells, several of them were further analyzed. In the process, they were vented and flood with electrolyte, overcharged for about 200 percent and then discharged with a reference electrode present in order to obtain a measure of the electrochemical activity of the positive and negative electrodes separately.

And the next graph shows a plot of a discharge of a typical cell from one of those batteries.

(Slide 63.)

The upper curve shows the cell voltage. The cell voltage comes down here. There's a small knee here and then continue down and flattens out down here.

As indicated here, we measured the negative potential with respect to the case and at the same time with respect to a reference electrode in the contact in the electrolyte in the cell.

And, as you can see here, the negative to case potential rose up and was pretty much a reflection of the cell voltage curve and on up there. The negative to reference voltage did some funny things here and then continued on up and flattened out as the negative electrode was completely discharged.

If you add up the ampere hours in this discharge for this 12 ampere hour cell -- I believe, say, this one was

approximately 16 ampere hours to this inflection point here. The fact that there was only a couple more ampere hours, if that much, of electrochemical negative capacity is subject to various interpretations. The one which is the one most easily to swallow, is that the electrochemical activity of the -- well, the assumption was made that when the cell was overcharged 200 percent that we charged up the negative electrode completely, so the fact that we only got about 10 percent more negative capacity than we got positive capacity, indicates obviously the negative electrochemical capacity has gone somewhere.

And so we postulated that what had happened was that the negative electrode had lost the activity -- the precharge had lost its electrochemical activity. And so in order to check this, we took the cell apart and did a chemical analysis of the negative electrodes.

I don't have that specific data to show you, but I can tell you that the chemical analysis showed essentially no charged negative material. On the other hand, it showed the total chemical cadmium activity as about what would be expected in this size cell, considering what was known about the initial ratio of positive to negative loading that was in these cells.

So right now I'm not quite sure what the explanation -- how to put all of these facts together. There's still a question in my mind as to why we only measure slightly more electrochemical activity in the negative in the positive and yet the chemical analysis shows something like 50 percent or more cadmium activity.

Maybe someone here might be able to comment on that.

Let me show you one other slide is a similar plot of a similar test on one of the cells that had been stored shorted, for which we got a normal expected charge voltage behavior.

(Slide 63a.)

And except for the fact that there's a little more difference between the point where the positive cuts off and the point where the negative runs out of gas, there's still, there's a very low ratio of negative electrochemical activity to positive electrochemical activity in this cell.

This cell also analyzed for approximately a normal amount of cadmium material from a chemical standpoint. So, again, I can't explain these results, but I thought, initially that the behavior of the cell before opening and this discharge curve might simply be a reflection of the

DRY 89 HOUR 0000 - 777 SPECIAL CELL EVALUATION - PACK 7

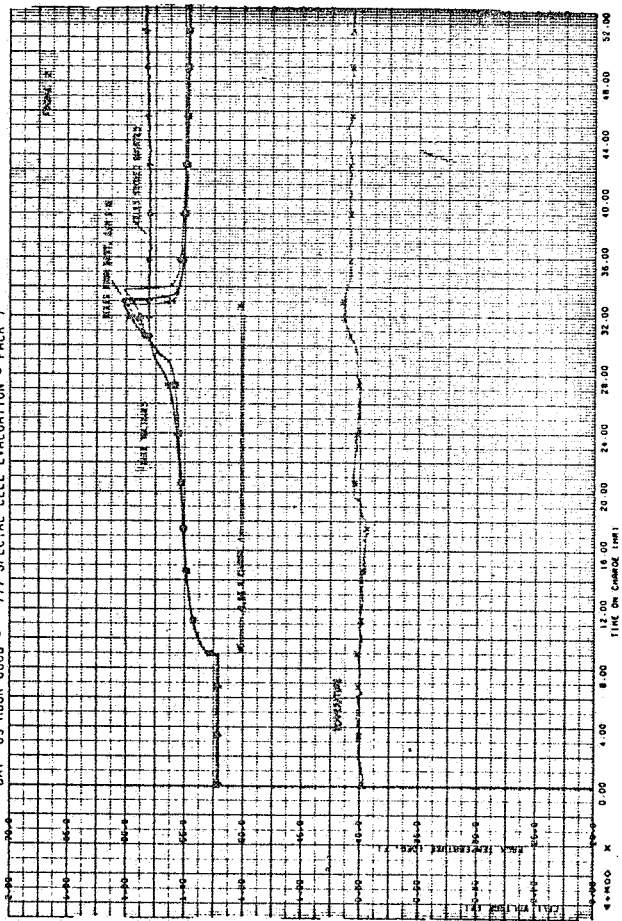


FIGURE 62B

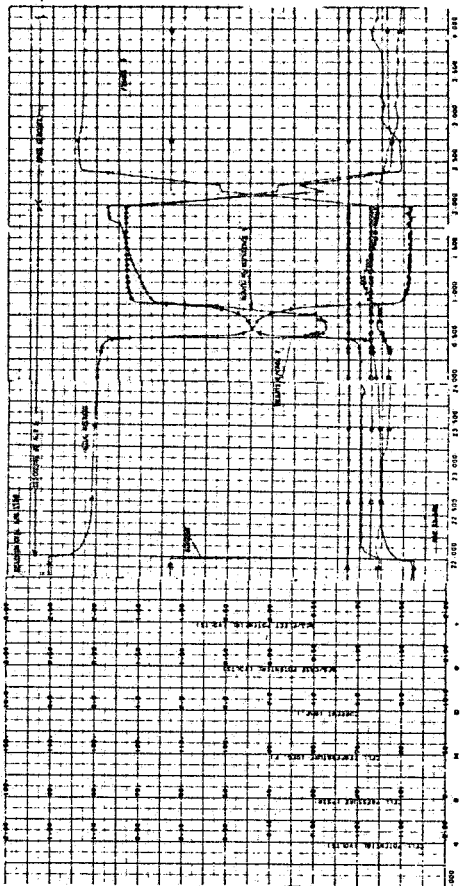


FIGURE 63

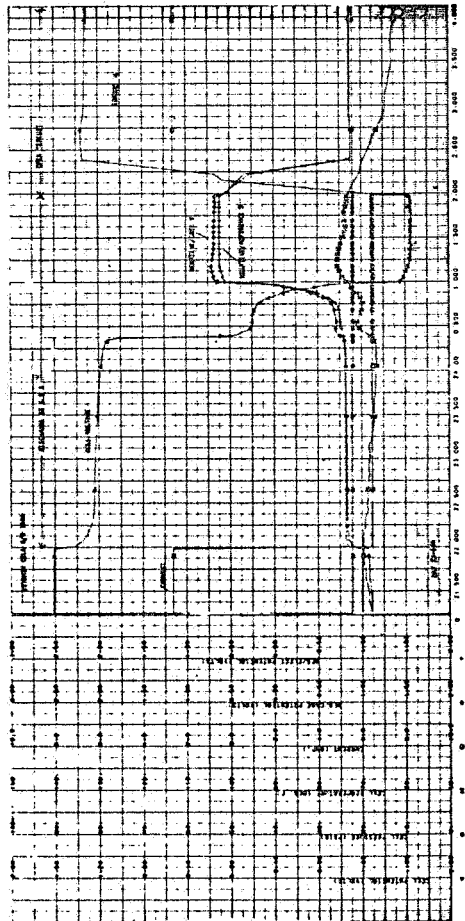


FIGURE 63A

fact that the cell had lost the electrochemical activity of the precharge. But the results don't seem to bear that out.

And so that's what I had to say about that.

FORD: Questions?

SEIGER: What was the end of charge of voltage as you charged the flooded cells?

SCOTT: Well, it was highly variable, but in the range, ranged from a little over 1.5 to 1.56 volts, different cells.

SEIGER: Let me make a comment on some observations that we have in formation in which we know that the capacity is built in and is usable in the negatives and it's about 50 percent more than the positive.

And we had doubled the ampere hour capacity input to put into the negatives to get it fully charged and we found that the voltage was still low, somewhere in the order of 1.5, 1.52.

So we changed our process in which we required that the voltage step up to about 1.6 volts and we find we have to charge for about $6\frac{1}{2}$ hours or 7 hours at which time we are able to get the respective capacities of the negatives and our conjecture is that perhaps there is so much electrolyte being pushed down that we are getting an inefficient charge of the negative electrode in spite of the fact it is flooded in formation and that some of the oxygen and gas is being reprovided.

SCOTT: At what rate are you talking about charging?

SEIGER: This is a C over 2 rate.

DUNLOP: Did you take any of these cadmium electrodes out and run them in a flooded bath?

SCOTT: No, not outside of the cell.

DUNLOP: That's a pretty good way to find out if the utilization of cadmium is really gone or if something's happening inside your cell.

SCOTT: Yes, right. We were somewhat constrained, as often occurs in this kind of a thing and also we wanted to do this under the conditions that we had been doing so-called electrode capacity test that is included in our cell acceptance

tests, which involves charging the cell in a flooded state in the original case. And I know that there's always a question of whether the negative electrode is fully charged under this condition.

And maybe it was not and -- I mean, that's the only other good explanation I guess that there is for our observations here.

DUNLOP: Well, let me ask you another question. When you say there was 50 percent more cadmium -- I think that's the ratio, 1.5 to 1 volt or something -- is that the amount?

SCOTT: Yes, approximately.

DUNLOP: Was that based on the total -- in the analysis the total cadmium available for the analysis?

SCOTT: Total cadmium to total nickel active.

DUNLOP: Yes. You would expect probably 65 percent utilization of that cadmium electrode roughly?

SCOTT: Yes.

DUNLOP: Does that add up or is that way off? I didn't get your numbers.

SCOTT: Well, I guess I don't quite follow you.

DUNLOP: What was it -- 30 ampere hours of cadmium total, if it were all electrochemically utilized?

SCOTT: No, it would be -- maybe more like it might be 24, 22, 24.

DUNLOP: That would be based upon the total cadmium?

SCOTT: Yes.

DUNLOP: What did you actually measure?

SCOTT: Electrochemically?

DUNLOP: Yes.

SCOTT: About 18 and 19.

DUNLOP: That's really not too bad, I don't think, in a way. We normally don't find even when we flooded them that after we have run them for some period of time, you never get much better than 68 percent utilization after, say, a year or two or operation of cadmium electrode.

SCOTT: That's a good point. But how about when they're new?

DUNLOP: When they're new you get up as high as 78, by the time we run 30, 40 cycles, it's down to 70 percent.

FORD: Other questions? Okay, thank you. Okay, I think seeing as it's the afternoon period, I think we'll take a ten or fifteen minute break and there is coffee in the rear of the building, if you'd like.

(Whereupon, a short break was taken.)

FORD: Our next subject deals with electrochemical impregnation, plaque materials and centered plate nickel outside electrodes and also electrochemical impregnation of centered plaques.

We have three speakers and they will be speaking along the same general subject. At this time I'd like to introduce you to Mr. Dave Pickett of the Air Force Aeropropulsion Lab. His discussion is on electrochemical impregnation of nickel plaques with cadmium and cadmium hydroxide. Dave?

PICKETT: During the past three years we've conducted an in-house program at the Air Force Air Propulsion Lab on fabrication of nickel and cadmium electrodes using an electrochemical impregnation techniques.

At the past two NASA/Goddard workshop meetings, I've presented data on the electrochemical impregnation of the positive plate. At this time, I'd like to present some of the work that we've done on the negative.

I'd like to also say that a report will be forthcoming soon on both of these processes. Electrochemical methods are cathodic in nature and similar to those developed at Bell Labs by Beauchamps and co-workers.

These methods are being further developed for production of space cells by Heliotek and Vince Puglisi will present some of the work done on that.

If I can have the first slide, please?

(Slide 64.)

On a beaker level the process is easily demonstrated. What one does is use a plaque for a cathode and cadmium metal as anodes, immerse this in a solution of cadmium nitrate and

pass current through the solution. As a result of the reduction of the nitrate, hydroxide ion is formed and the cadmium is precipitated inside the plaque.

(Slide 64a.)

The general procedure for this is outlined on the first slide. What one does is heat the solution almost to boiling, then cathodize. We used 1.4 to 1.6 ounce per square inch of plaque for ten to fifteen minutes. We have used less time then that.

We used pure cadmium anodes. This is where we differ in one respect from the Bell process. They use inner anodes and use a sodium nitrite additive. Once the plaque is impregnated, it's removed and cathodized in 20 percent KOH at .55 amps per square inch for twenty minutes and this is carried out at about 80 degrees C.

We saturate the KOH with cadmium hydroxide to prevent loss of the hydroxide from the plate in solution. We reverse the polarity and sometimes we repeat steps three and four several times.

This helps to remove the external scale on the surface of the plaque. The excess is then brushed away and then dried at 35 degrees in a vacuum oven, preferably overnight.

Okay, let's see the next viewgraph, Floyd.

(Slide 65.)

This shows what the voltage looks like if the impregnation is carried out. During the impregnation a cadmium hydroxide film is formed on the anode and increases the resistance of the impregnation bath and this is apparently the reason why the slope is going up on the curve.

One also gets cadmium as well as cadmium hydroxide deposited inside the pores of the plaque.

Okay, and if I can have the next slide I'll show the plaque material we used.

(Slide 66.)

On this data that I'm presenting here -- this is Eagle Picher plaque. The pore distribution is an estimate from this picture here runs somewhere between five and eighteen microns in diameter with an average of somewhere around twelve.

Okay, on the next viewgraph I have some data which I obtained from 3 x 3 plates, inflated cells and I've compared

NEGATIVE PLATE IMPREGNATION PROCEDURE

1. HEAT 1.5-2.0 Molar CADMIUM NITRATE SOLUTION TO 100°C.
2. CATHODIZE SINTERED NICKEL PLAQUE IN ABOVE SOLUTION AT 1.4-1.6 AMPS. PER SQUARE INCH OF PLAQUE FOR 10 TO 15 MINUTES. (PURE CADMIUM ANODES USED).
3. REMOVE PLAQUE AND CATHODIZE IN 20% KOH AT 0.55 AMPS/IN² FOR 20 MINUTES (KOH SATD. WITH Cd(OH)₂).
4. REVERSE POLARITY AND REPEAT STEP 4.
5. BRUSH AWAY EXCESS DEPOSIT THEN WASH.
6. DRY AT 35°C IN VACUUM OVEN.

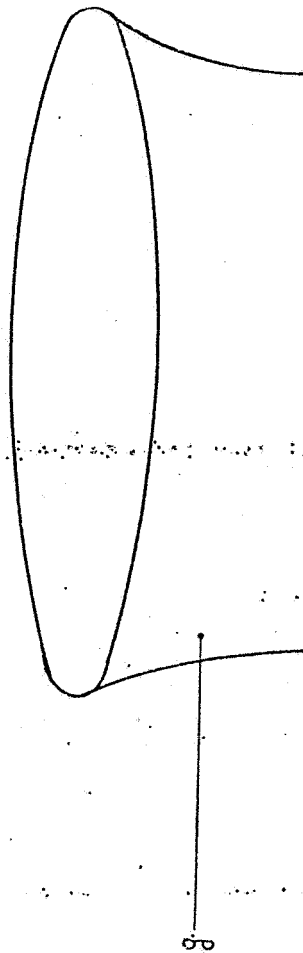
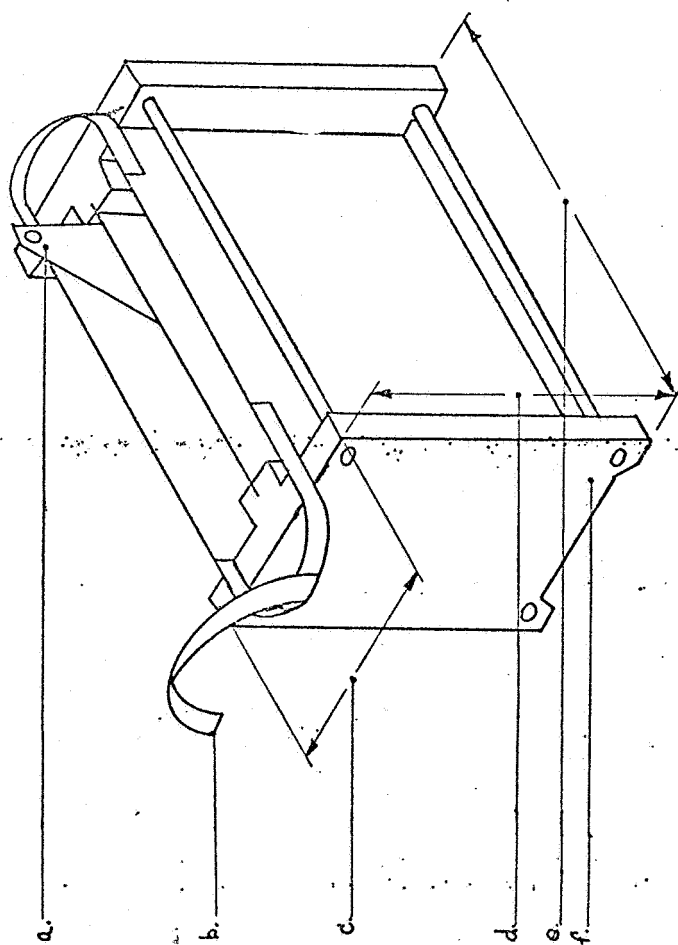


FIGURE 64

FIGURE 64A

this with some plates that I've taken from aircraft batteries.

(Slide 67.)

These are 12 amp charge or about the 3C rate and 1.5 C discharge at 50 percent overcharge. These first results were carried out at about 30 cycles to evaluate the plates to see how they performed as compared to state of the art variety.

(Slide 68.)

The next viewgraph shows a comparison on the basis of weight. You'll notice that the electrochemically impregnated plate seems to be a bit flatter with an increasing cycle number than the commercial plates.

But one cannot tell very much just from 30 cycles only. We had as high as 83 percent utilization of active material in this process and in these cycles here the utilization ran from about 70 to 83, with an average of about 79 percent in flooded cell.

Okay, we scale this process up to producing -- let's see there's 2-3/4, about 4-3/4 of electrodes -- and I believe the apparatus for that is on the next slide.

(Slide 69.)

This polypropylene tank and you have alternating anodes and then plaque. This is connected to a 300 amp power supply and the solution is circulated through the tank. It enters the bottom and comes out the top and the vapors are condensed with the condenser on top.

(Slide 69a.)

The next slide, I believe, 33 mm. slide, shows how the circulation proceeds. It goes through a heater, is heated, and then returned to the tank and the tank, if it's brought up to about 100 degrees with the immersion heaters, the heater doesn't quite get it to that temperature.

(Slide 70.)

Okay, on the next viewgraph, I have some of the results of the impregnation from the scale up. Our initial results yielded about 1.7 to 1.9 grams of active material per cc. of void and you have to remember that some of this is in the form of cadmium and some is in the form of cadmium hydroxide. (See bottom of Slide 70.)

VOLTAGE-TIME PLOT FOR ELECTROCHEMICAL
IMPRESSION OF NICKEL PLATES
WITH Cd AND $Cd(OH)_2$

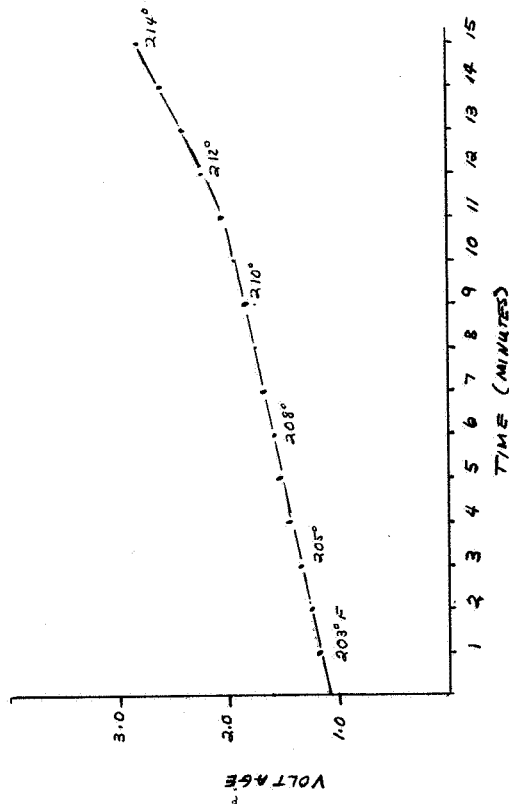


FIGURE 65

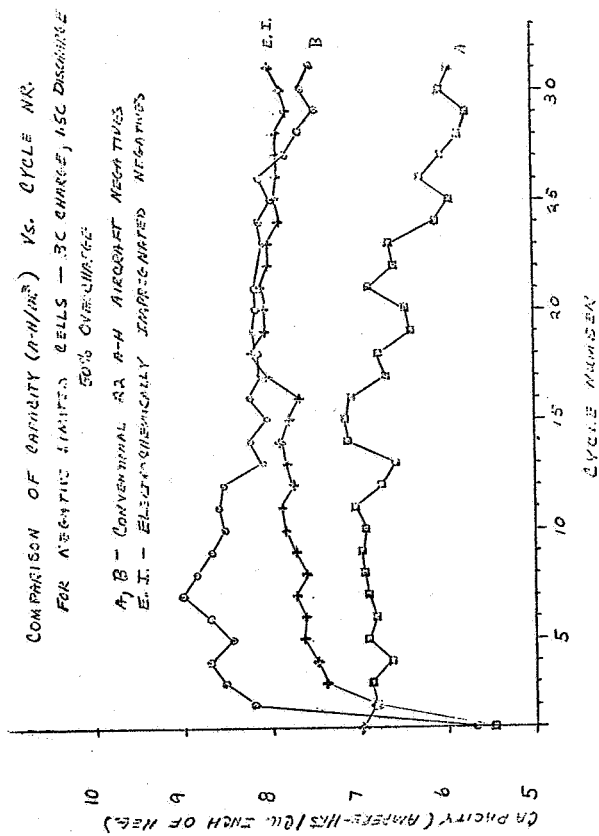


FIGURE 67

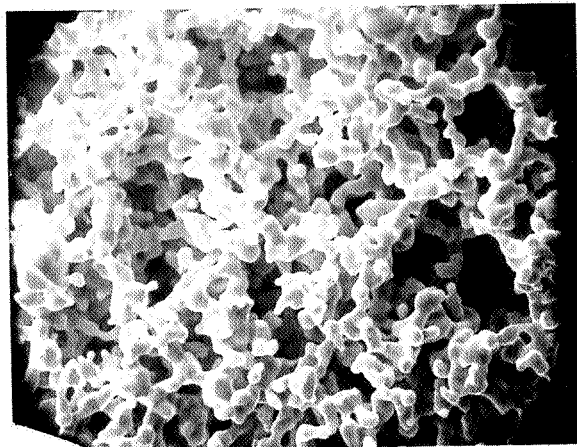


FIGURE 66

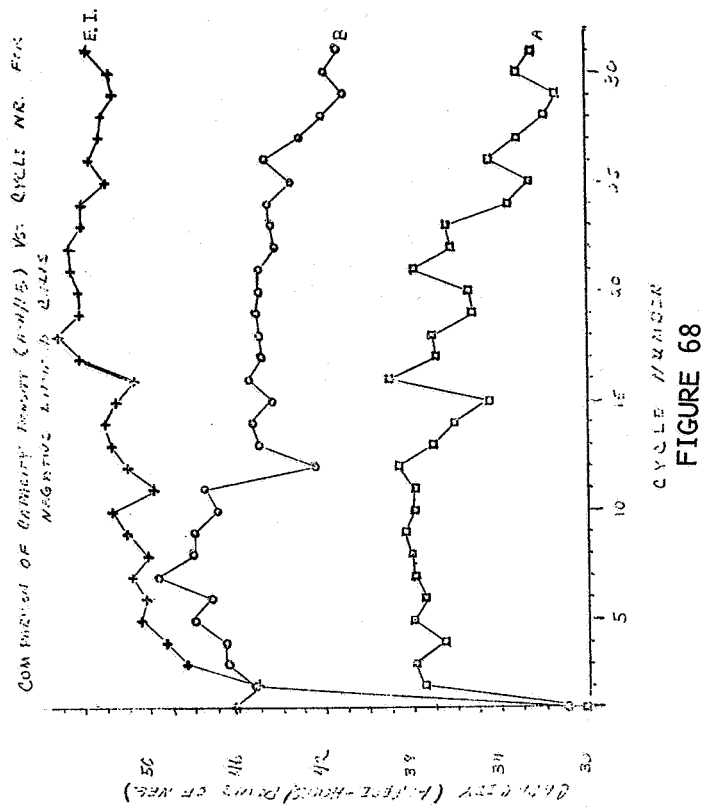


FIGURE 68

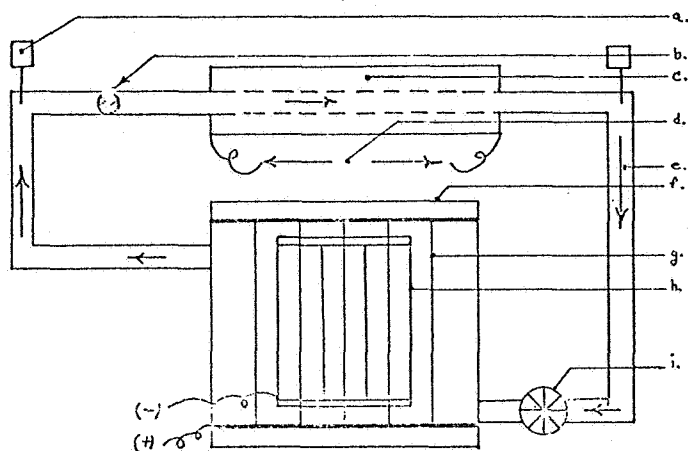


FIGURE 69A

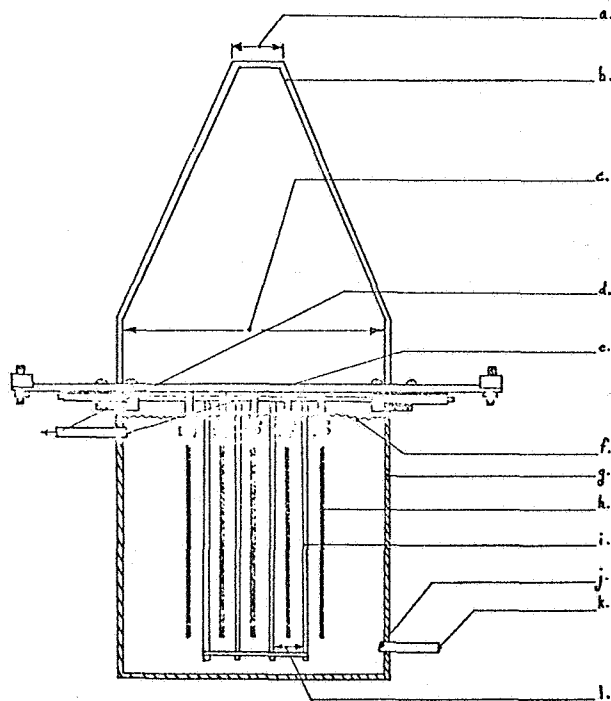


FIGURE 69

SCALE-UP LOADING CHARACTERISTICS OF
CADMIUM ELECTRODES FROM ELECTROCHEMICAL
IMPREGNATION FROM AQUEOUS NITRATE SOLNS.

(9.50" X 8.25" X 0.020" PLAQUES INCLUDING
SIX 2.75" X 4.75" ELECTRODE AREAS WITH
0.20" COILING BETWEEN AREAS, 0.100" ON EDGES)

PLAQUE #	WT. OF DEPOSIT	WT. OF MATL PER CC VOID	THEO. * CAPACITY	THICKNESS (IN.)
20-1	41.10 gm	1.86	9.25 A-H/M ²	0.0001
20-2	36.80 "	1.70	8.48 "	-0.0003
20-3	37.60 "	1.72	8.57 "	0.0002
20-20	51.60 "	2.18	11.51 "	-0.0001
20-28	51.87 "	2.31	10.79 "	-0.0003

* - ASSUMING 20% Cd, 80% Cd(OH)₂ COMPOSITION OF ACTIVE MATL.

FIGURE 70

And I've given a theoretical capacity for these here. Our later results looked a little more promising. We got as high as 2.3 grams of active material per cc. of void in these.

Okay, and I have some cycle data, I think, on the next viewgraph --

(Slide 71.)

-- of some 20 ampere hour cells we made from a scale-up process. These were made from the plates of the first batch -- I've shown you there -- the higher loaded plates we have not tested as yet.

The aim here is a constant potential charge at about 1.7 to 1.9 volts and the reason for using this voltage is so we can get all of the charge in in about an hour. Then it is discharged at about the one hour rate.

We started these out at about 70 degrees and varied the temperature on them and we went from 70 to 90, then we went to 110. The reason I have the dotted line there with 110 -- I'm not really sure that the capacity of the cell at this point is really dictated by the negative plate -- the positive plate becomes very inefficient at these temperatures and it might be positive limited.

After 760 cycles, the capacity fell off about 20 percent on these. Okay, then, take up much more of your time with this data -- I'll quit at this point -- and Vince Puglisi is going to talk about some of the work that he's done after Harvey Seiger talks about some sintering processes and what not.

In other words, there'll be some more data forthcoming on the work we've done with the negative process.

FORD: Are there any questions at this point on what Dave has presented? Mr. Kroger, from General Electric?

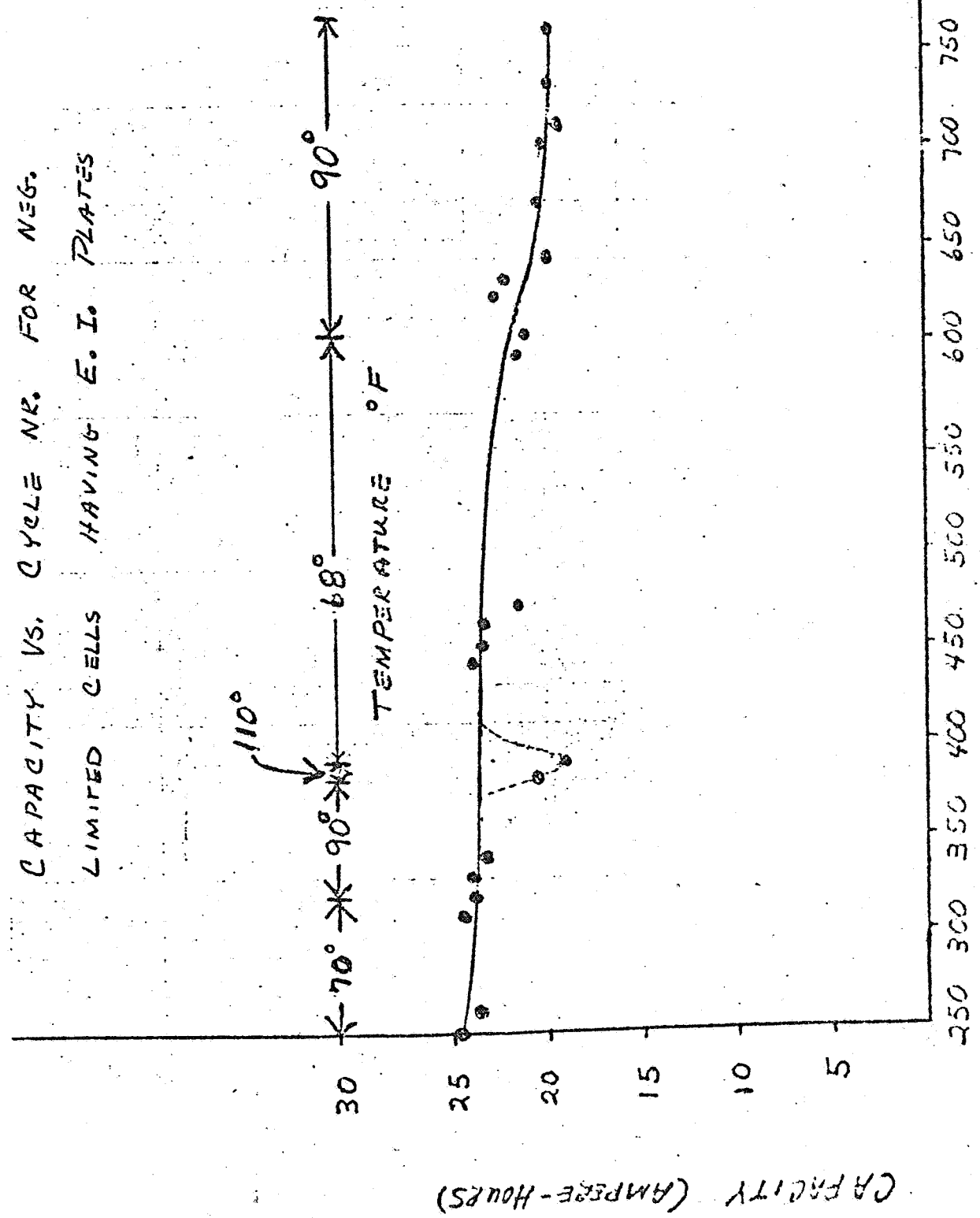
KROGER: How many times do you maintain the constancy of your pH data?

PICKETT: We don't really worry about it too much, Hans. What we do is we usually set it about four and then after the impregnation, it'll get up to saturation point, in other words, greater than five.

And we regenerate the solution for the next impregnation by simply adding nitric acid.

KROGER: You don't do anything during the run itself?

CAPACITY VS. CYCLE NR. FOR NEG.
LIMITED CELLS HAVING E. I. PLATES



CYCLE NUMBER

FIGURE 71

101a

PICKETT: No.

FORD: Keith (Mounds)?

MOUNDS: The number you are showing -- ampere hours per cubic inch for that negative -- were they after formation or before formation?

PICKETT: These are based on the loadings that we got there, assuming that we have 20 percent cadmium deposited in the plate and 80 percent cadmium hydroxide and this is just after impregnation.

MOUNDS: We found by analysis that the deposit is about 98, 99 percent hydroxide plus a tetra basic cadmium nitrate compound. The geometry is a little variable. We found the only reliable number we could use was weight gain after formation or preferably a cadmium analysis.

PICKETT: The reason that I used the 80/20 ratio is based on the data that I showed with the beaker level plates. I took the weight immediately after impregnation and then ran 30 cycles on them and weighed them again.

And then on the basis of this, I made the calculations and that's the reason for my assumption on the large scale.

MOUNDS: Your utilization might be a little higher than what you calculated.

PICKETT: That's true.

FORD: Any other questions? Thank you, Dave. Okay, the next topic is to be presented by Dr. Harvey Seiger of Heliotek, Textron. The subject is plaque materials for sintered plate nickel oxide electrodes and this work and the presentation is co-authored by Vince Puglisi and Paul Rediman. Harvey?

SEIGER: I will be talking about the plaque materials and the impregnation of positive electrodes and will be covering both the immersion methods as well as the electrochemical deposition that Dave was just talking about.

And Dr. Puglisi will later discuss the electrochemical impregnation of both positives and negatives. And this is essentially a continuation of some of the work that was talked about last year at the workshop on sintering.

And there are three sub-topics that I wanted to cover on the plaque materials and make these points. One is on direct experimental evidence that the utilization of active material in the positive electrodes is dependent strongly on the sinter porosity.

And then I'd like to go into some conjectures. For instance, there appears to be some upper levels of impregnation of positive electrodes beyond which one shouldn't want to go and the numbers appear to be somewhat different depending on the process.

And then thirdly we want to talk about a hypothesis that'll cover and explain why plates do blister and why they thicken, particularly positive electrodes -- as we charge and discharge them there are changes in dimensions and I was wondering how to stop Floyd Ford this morning.

He almost made null and void the last part of my presentation. And I'd like to point out that these topics are important when we design plaque for cells when we're targeting on 20 watt hours per pound or more.

Now, there are -- it appears that one can divide the impregnation processes up into two groups. In one group we see values of impregnation, utilization of positive material in excess of 100 percent. In the other types, there're less and the methods that I'm covering today will be dealing only with those that do yield a higher value of utilization.

Now, I think I'd like to have the first slide, please.

(Slide 73.)

And a very interesting one because there are five data points on there or there appear to be five data points on there. It's a plot of the utilization that one gets of the negative active material on the third formation cycle when it's flooded as a function of the sinter porosity and I'll always talk sinter porosity.

That is, I'm not going to be concerned with the grid that's in there and its effect upon the apparent plaque porosity, so I'll always talk sinter porosity. In fact, there are more than just five data points.

A little bit of identification of them -- do we have a pointer? Well, we started back in 1970, we kindly

got some plaque material from several sources. One source was Gould, who supplied us with material that was 72 percent porous. Marathon was very kind and supplied us with some material that was 82 percent porous and after we had done our work with them, we decided that when we make our plaque, we want about a 75 percent porous plaque for our positives and about 78 percent porosity for the negatives.

And so we eventually made them and then we impregnated both as positive electrodes and here are the data. This data point was loaded to about 1.4 grams per cc., similarly went back to about 1.4, 1.5. These were done by several methods with molten salt and with an aqueous impregnation up to values between 1.4 and 1.6 and then also electrochemical taking them up to about 1.9.

The last value on here is one that Dr. Kroger reported to the Air Force under their report using the constant potential method and he loaded to about 1.8 grams per cc. and he had a porous plaque, quite porous, and I used his number, putting it right on.

It seemed to fall in. So, I feel that there is a definite dependence and a linear dependence over this range between sinter porosity and the utilization that one gets. And I think that this slide demands several comments.

Perhaps the first one is very interesting. Dr. Kroger reported that he added some lithium hydroxide and once he added the lithium hydroxide to his 20 ampere hour plates, the utilization scooted way up -- I believe the number was 118 percent.

And so we went down into one of these and we put some lithium hydroxide in and we got just a little bit. And now perhaps we have some indication of why there are divergence of reports on lithium hydroxide.

It's a little premature -- only two data points -- but perhaps there's a rotation of this curve, of this utilization curve, so that if one has a very porous plaque, one will get quite an effect, a significant effect by adding lithium hydroxide but at lower ends the utilization will be virtually unchanged and this may square away some of the differences that we see in the literature with the effect of lithium hydroxide on utilizations.

I'd also like to point out that a pore former was used in making the 75 and 78 percent porous centers and one

FIGURE NOT AVAILABLE

DEFINITION OF NON-RIGOROUS PORE DIMENSIONS

ASSUME A PORE WHICH IS AN OPEN ENDED CYLINDER IN WHICH THE DIAMETER IS λ AND THE LENGTH IS l :



A SAMPLE OF PLAQUE CONTAINS n SUCH PORES. THE SURFACE AREA OF EACH IS GIVEN BY S AS:

$$S = 2\pi \left(\frac{\lambda}{2}\right) l = \pi \lambda^2 l$$

AND THE TOTAL SURFACE AREA IS GIVEN BY \bar{S} AS:

$$\bar{S} = n\pi \lambda^2 l$$

THE PORE VOLUME IN EACH IS GIVEN BY V AS:

$$V = \pi \left(\frac{\lambda}{2}\right)^2 l = \frac{1}{2} \pi \lambda^3 l$$

AND THE TOTAL SURFACE AREA IS GIVEN BY \bar{V} AS:

$$\bar{V} = \frac{n}{2} \pi \lambda^3 l$$

λ IS DEFINED AS THE NON-RIGOROUS PORE DIMENSION:

$$\frac{\bar{S}}{\bar{V}} = \frac{n\pi \lambda^2 l}{\frac{n}{2} \pi \lambda^3 l} = \frac{4}{\lambda}$$

WHENCE $\lambda = 4 \frac{\bar{S}}{\bar{V}}$

FIGURE 74

UTILIZATION OF PORES, ACTIVE MTI, % (E)

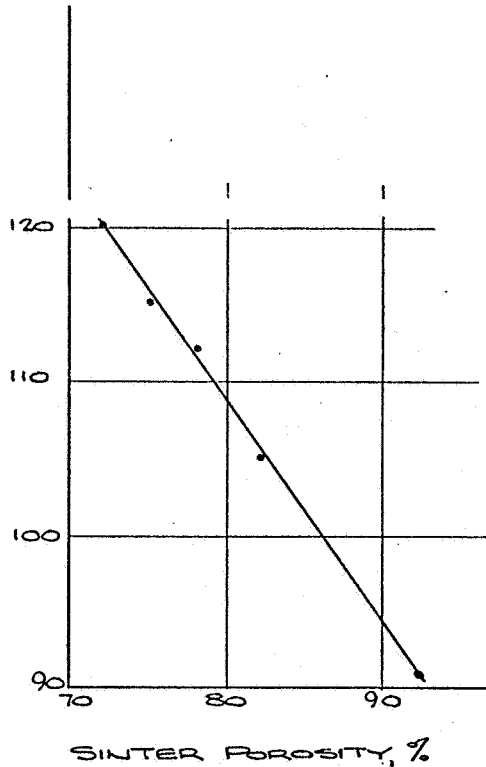


FIGURE 73

THE NON-RIGOROUS PORE DIMENSIONS FOR REAL PLAQUE

SAMPLE #	VOID VOLUME CM ³ /IN ²	PLAQUE WT GM/IN ²	VOID VOLUME CM ³ /GM	SURFACE AREA CM ² /GM	" λ " MICRONS
SAMPLE #4	.291	1.159	.251	896	12
SAMPLE #9	.278	1.171	.287	928	10
MARATHON	.271	.756	.358	428	33
GOULD (WIRE MESH)	.294	1.022	.249	748	13
GOULD (PUNCHED FIL)	.261	.987	.264	984	11
TYCO (29 mil)	.225	.755	.298	854	14
TYCO (50 mil)	.269	.957	.272	889	15
ENGLE PAPER	.866	1.024	.857	1,022	17
GULTON	.846	1.149	.801	818	15

FIGURE 75

104a

might suspect if you add a pore former or something that you put in to hold pore and then you burn it off later, you may be winding up with two different pore size distributions.

And we gave that a little bit of thought and let's go to the next slide.

(Slide 74.)

We said to ourselves, "We've been getting some data on pore volume that we call grams of void per square inch of -- pardon me, cc. of voids per square inch of plaque -- and we're getting surface areas that we're doing with a pulse method using the electrochemical capacitance method.

And we have these data and we made an assumption on what a pore might be and it doesn't make much difference what we call a pore. This will go into the transcript. Let me say that we call, we define a pore parameter as L , which has some relationship to the size of the voids that we have in the plate.

And that microscopic number is related to these two macroscopic numbers, the void volume, and the surface area within the plaque. And I'm going to go back to some data that we had last year, which were recalculated and are given in the next slide.

May I have that?

(Slide 75.)

I made a selection since sample no. 4 and sample no. 5 were Heliotek plaque. We took those two -- one is a formulation similar to that sintering condition similar to that we want for our negatives and might for our positives.

So we took those and we looked at some of the others. And we had all of the measurements that were reported last year and all we did was calculate the last column now, the L value, which says that the pore dimension appears to be about 10 to 15 microns.

I think that agrees with a number we heard a little while ago, even on the Eagle Picher plate in which Dave said he measured about 12 microns. So it's a slight order of magnitude, right kind of ballpark.

There's one number that appears to be out. We've had some other numbers that were calculated that I didn't present. I took only those that were interesting and there was

something peculiar about the form in the capacitative charging up of the double layer of the Marathon and I don't know whether that's a real number or whether that's an artifact. It may have been so old, I'm not going to pay much attention to it, but it does look like we all have the same kind of pore size even though several of them, at least sample no. 4 and sample no. 9, do have pore formers around.

Well, I have one more comment to make on the first slide. We physical chemists have all been frequently accused of wanting to plot data so that we'll always get straight lines and we never really expect a simply plot like this to come out to be a straight line, so I want to upset it.

I want to now make it not a straight line and I'm going to do something about that. Let's consider what we have. There are pores. We load the pores up to a level of L .

Now these pores which we'll call V , multiplied by L , gives us a theoretical capacity. We'll say $C=LV$. Now, to get that third formation capacity, we have to multiply it by a utilization, which we'll call ϵ .

And so, to get that third value, the capacity on that third formation cycle, will be $L \cdot V \cdot \epsilon$. May I have the next slide?

(Slide 76.)

And there it is. That's the top equation. Now, we have an equation for ϵ from the first slide, which is $A-BP$. And now we can throw in yet another equation and we define the void volume in terms of porosity.

And the porosity is equal to the void volume as a ratio to the total volume of the plaque, only we correct it for the grid that's in there, and we subtract it out. And that is our definition of the void volume.

And, now, if we substitute the two equations into the first one, we'll see that we have a second order equation in the porosity and if one has a second order equation in the porosity, then we can do a little bit of differentiation and come out with the fact that there is a maximum capacity per unit volume of positive plate which is a very nice number.

And it says that that maximum occurs at a 78 percent porosity plaque. And so we see here that the maximum porosity occurs at .78 or 78 percent porosity plaque, but that

doesn't give us an answer as to the other number that we're interested in, not watt hours per cubic inch, but watt hours per pound, and in this case, ampere hours per pound.

And that's more complicated, because every time you make a change in the positive electrode, you make a change in the capacity, you make a change in the negative electrode, you make a change in the loading, you make a change in the separator and it becomes -- there are about five items that have to be considered, so it can't be done in a straight, analytic fashion, as we're able to handle the capacity per unit volume in the positive electrode.

All right, that's enough of that slide. I'm going to talk about some loading limits. And there does appear to be some practical upper loading limits in the electrochemical impregnations we find we can fill those voids to about 2.5 grams per cc., but the plates thicken.

And if they thicken, then the final number after impregnation has to be calculated on what you're going to build into the cell and what it thickened to. So all the numbers have to be revised for the swollen void volume.

Although we talked about loading -- the previous information has been loading based on the initial plaque porosity -- we're interested in what the capacity is that we drop into a plate into a cell.

And Vince a little later will show that loadings above about 2.35 grams per cc. is likely to cause -- probably not likely -- but the probability of getting blisters apparently increases as we go above a loading level of 2.35 and consequently with the thickening that goes on, we want to control ourselves to below 2.35 and appears that by the time thickening occur after formation, that our actual loading levels will be down in a range of about 1.9 to 2.1 grams per cc. and that will about minimize thickening.

We will still get thickening and I'll discuss that. But before I get onto thickening, I should mention one other fact and that is we've been finding that the third formation capacity is greater than that value that will obtain in a cell.

And the cell's value is about 85 percent of the third formation. I think that that's a pretty fair number for us to be using for the design of cells. And in this third area I want to talk about a hypothesis of blistering and of thickening.

And here I'm going to emphasize somewhat the immersion method. And in the immersion method we take the nickel

nitrate, hexahydrate, we get it into the pores, into the voids and then we dry it and run through a conversion to nickel hydroxide.

And one might ask, "Well, how can this give rise to blisters? We're looking for stresses inside. We're looking for differences in volumes and if we looked up the values of nickelous hydroxide, the density of nickelous hydroxide and the density of the nickel nitrate or the nickel hexahydrate, one finds that, the hydrate is more dense than the nitrate. It's not going to blister. It's not going to produce any stresses."

And so we scratched our heads a little over it and then we ran a simple experiment. May I have the next slide?

(Slide 77.)

What we did here was set up an experiment ala Dr. Case in a test tube, in which we took some nickel nitrate that was molten and we dehydrated it and we also took some fused nickel nitrate that we didn't dehydrate.

And we converted it with various concentrations of potassium hydroxide, ranging from 30 percent down to 10 percent. And the material that was not dehydrated, we treated with 30 and 15 percent.

And we made two observations. One was how flocculent is it? Because if it becomes flocculent, then it's more dense than the data in the books. So, we're dealing with hydrated oxides.

And the observation is that as one decreases the concentration of the potassium hydroxide in the conversion, the density becomes greater in the hydroxide. If you're not dehydrated, it becomes even more flocculent.

One looks at the color, we start with the green and it starts tending to go over to a blue, so in this fourth case it's mostly blue and some green. So we are dealing with different degrees of hydration of materials and not only that but it appears that the nature of the hydroxide that's used for the conversion is also important, because if one were to take a 15 percent sodium hydroxide solution, then one finds that there's a green precipitate that's only slightly flocculent.

And so you can avoid some blistering by conversion in sodium hydroxide rather than in potassium hydroxide or use

a more dilute one. Be that as it may, we've learned some things from this and that is if we have a hydrated nickel hydroxide, as we keep impregnating with each cycle, the stresses that are occurring inside the plate are building up and a probability of getting blisters are increasing.

I'm going to neglect the case of overcharge or over-discharge where there are a lot of gases. I want to stay with the chemical methods, because it seems that they are important when the cells are being made right at the beginning.

And I don't want to weaken the plaque. We've been using a strong plaque. We've been going through the use of pore forms to have a strong plaque. I don't want to lose that characteristic.

We want to stay under conditions where we stress minimally. So as one keeps loading a plate up greater, the probability of encountering blisters will increase and, as I said, if we avoid any of the hydrated nickel oxides, it appears that we can avoid blistering completely.

We have several things that we can consider, for instance, if we want to offset stresses. May I have the last slide?

(Slide 78.)

I think this will clear up some of the points. We're dealing -- the one on the left is in a scanning electron microscope photograph of a sintered nickel plaque and this one happens to have been made with pore former. We can't find too large distribution of pores.

We can find two pore sized distributions -- a larger one and a very small one, but we can't find two large ones, which would correspond to the pore former like we've added. The one on the right is the same kind of plaque that's been impregnated as a positive electrode.

And the interesting thing about this is that the nickel hydroxide -- and this is nickelous hydroxide, but it's black, it's been reduced, so it's not hydrated. These little boulder-like, moller-like materials appear to be right on the sintered nickel that they are adhered to rather than within the voids.

So we look up here and we still see an open region. We see open regions here. We look at nickel hydroxide and it

$$C = L.V.E$$

$$E = a - bp$$

$$\text{BUT } p = \frac{V}{St}$$

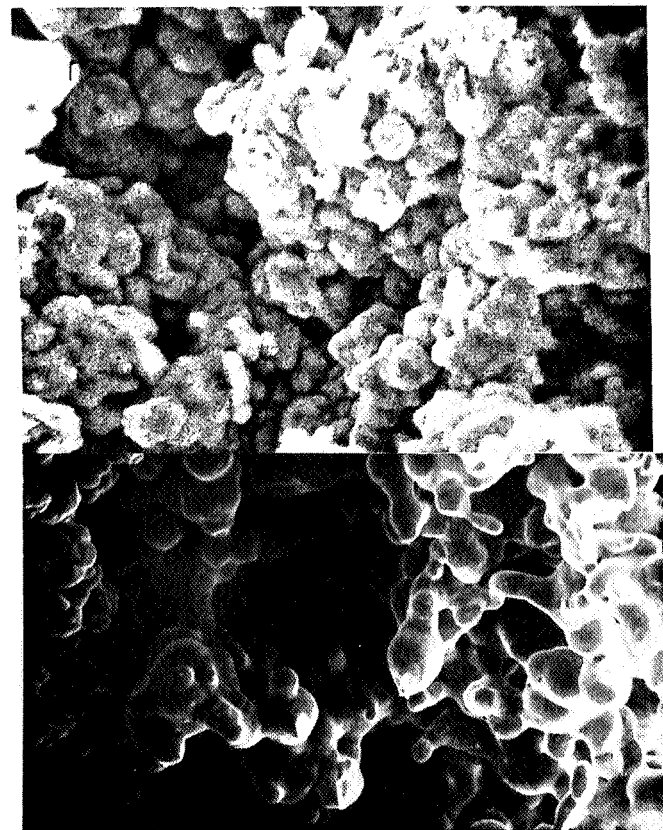
$$\text{HENCE } C = L(st)p(a - bp)$$

$$\frac{C/(st)}{L} \text{ IS MAXIMUM AT}$$

$$p = \frac{a}{2b} = 0.78$$

$$\text{SINCE } \left(\frac{\partial C/st}{\partial p} \right)_L = a - 2pb$$

FIGURE 76



LEFT RIGHT
FIGURE 78

CONVERSION OF SOLID NICKEL NITRATES
WITH
AQUEOUS KOH SOLUTIONS

NICKEL NITRATE	CONC. KOH, %	VOLUME	COLOR
Ni(NO ₃) ₂	30	FLOCCULENT	GREEN
Ni(NO ₃) ₂	22.5	INTERM. FLOC.	GREEN & SOME BLUE
Ni(NO ₃) ₂	15	SLIGHTLY FLOC.	BLUE & GREEN
Ni(NO ₃) ₂	10	SLIGHTLY FLOC.	MOSTLY BLUE & SOME GREEN
Ni(NO ₃) ₂ ·6H ₂ O	30	VERY FLOC.	GREEN
Ni(NO ₃) ₂ ·6H ₂ O	15	SLIGHTLY FLOC.	GREEN & SOME BLUE

FIGURE 77

sure looks as if it's being placed on top of sintered nickel and if it's placed on top of sintered nickel, we can assume that it's going to stay that way.

And now there is a volume change as one goes from a charge to a discharge, if we look up the nickel hydroxide and the beta nickel hydroxide -- beta nickel hydroxide is 4.6, nickelous hydroxide has a density of 4.15 and these are the stresses.

Stresses, apparently, have to be related to how much material is in the pore. So, if we continue loading, these are expected to be larger. The stresses are expected to be much, much greater. I didn't do any of the mechanical calculations of how the stresses are increased by the degree of loading, but we kind of expect something more than a simple mathematical function.

And the changes between charge and discharge will govern the thickening of a plate -- a fully charged plate and a discharged plate. Now, since we are undergoing stress changes -- and it's a hoop stress that we see in there.

Since we are undergoing changes in stress, we would expect that there'd be some fatigue and that if we make a stronger plaque, it should last somewhat longer. Of contrariwise we might want to load to a lesser extent so that it would last longer.

We're not going to avoid -- it appears to me -- overcoming the thickening and the stressing that we have because of the changes, the molar volume differences between the two states of charge. But, obviously, it will be related to the depth of discharge, the strength of the sinter and the degree of loading.

And we've chosen the point of making a strong plaque and merely delaying the thickening and the stresses that might yield failure, so our point of view is that with a goal of 21 watt hours per pound, we don't want to sacrifice on the loading.

What we'd rather do is keep the loading up and improve the lifetime of the cell by having a stronger plaque and we have been able to load even by the emergent plaques and make some changes.

Now, I have no long-term results to tell you at this time, but the degree of plate thickening appears to have been decreased so that there's only about a $1\frac{1}{2}$ ml. thickening after

27 C rate charges and discharges at values of 75 to 100 percent depth of discharge. In spite of the fact that we had plates that were 78 percent porous and loaded to about 1.9 grams per cc. after thickening. Thank you.

FORD: Thank you, Havey. Any questions at this time?

LURIE: Harvey, how did you measure porosity?

SEIGER: I weighed the plaque and that is one parameter since the density of nickel is 8.9 and then I impregnate the plaque with water and we skim off the surface until we have only micro-droplets. I use that for the void volume.

Incidentally, were we to do it all on geometry, the values come in pretty close, they vary. I don't see more than two percent and they jump up and down. I don't see any set difference between them.

I was looking up that for evidence of lock pores, of pores that can't be entered.

LURIE: I'd like to comment on that. We did use the methods that you are talking about and we went through several months study with careful statistical analysis of the data comparing that method with simply measuring the thickness.

There was a bias between the two methods. The bias was constant and the dispersion of standard deviation was actually less on the straight forward mechanical method. There was a two percent difference.

SEIGER: How old were the plaques? This makes a difference. Incidentally, it makes a difference whether you pull a vacuum and how old the plaques are.

LURIE: Production runs. Oh yes, this was all fresh material. I don't mean to imply that one method is better than the other, but there is about a two percent difference.

SEIGER: Yes, I was looking for evidence of blocked off pores and I couldn't promulgate it -- I couldn't bring it out -- negative data.

FORD: Dr. Scott?

SCOTT: Normally, the liquid absorption method for

measuring void volume is referred to as measuring interconnected void volume whereas a straight weight measurement would measure total weight volume. Are you saying that the difference between interconnected as measured and total pore volume is only in the order of two percent of these materials?

SEIGER: I think Mr. Lurie and I both agree on that.

LURIE: We're saying essentially that you have all voids that are accessible to the water. We interpret the difference as having to do with a surface phenomena. In other words, we just take a micrometer and we measure the thickness as the micrometer sees it.

This is not exactly the same physical form that the water sees when you essentially squeegee the excess off from the surface, we do see a constant bias.

SCOTT: In which direction?

LURIE: We get a slightly higher value than straight geometric.

FORD: Bacher?

BACHER: This is just a minor point. There's a two percent difference in overall porosity in a 75 percent plaque -- it's about a 10 percent difference in void volume.

LURIE: I'm not implying those are real differences. I'm saying that both of these methods measure the thing which we call porosity. If we went to mercury penetration, we'd get a third one which would not be exactly the same as either of the other two, but also we would call that porosity, which is the only reason I asked the question in the first place.

SEIGER: I've got the microphone so I'm captive. My comment -- we're interested in the voids that we can put in an active material, a nickel hydroxide or a cadmium hydroxide.

We're also interested in getting potassium hydroxide into those voids, after they've been impregnated and so I'd love that liquid method. I may be wrong in using water, but I like it. Dr. Maurer?

MAURER: (Bell Labs) I have a comment. We studied three techniques of the mechanical method -- the water pick-up, the mercury porosimeter on the same blocks or plaques and confirmed largely what you are saying.

The mechanical method is systematically of higher values than water pick-up and they are systematically higher than mercury porosimeter. We find that the amount of difference, many times, is related to the surface condition of the pack.

The rougher the surface of the plaque, the greater the deviation of the two methods. The water pick-up methods, being easy to do, is somewhat operator dependent -- just how they wipe off the excess water droplets. With some practice, a single operator could get very consistent results and we find that on plaques that have good surface conditions, the difference is about one percent between mechanical and water pick-up and perhaps a half a percent between water pick-up and mercury porosimeter.

Another question I had: in the utilization figures, what you are quoting, are you using a cobalt additive?

SEIGER: Yes.

MAURER: Beauchamps and I reported at the electrochemical meeting in Detroit -- some work we did on stress cycling of positive plates made by the electrochemical method and we found this stress cycle consisted of a tendency charge and discharge, and 100 percent overcharge on each cycle and we found that looking at the cycle life of plates that were plaques that were strong or weak.

The weak plaques were sintered at a very low temperatures and the high strength plaques at higher temperatures and we found no difference between the strengths and cycle life.

What we did find was that the amount of cobalt in the plaque had a very pronounced effect on the cycle life with no cobalt or the residual cobalt is nickel nitrate, which is about 1/10 of a percent.

We have a cycle life in the vicinity of 200 cycles and with five to ten percent as we move out to 1,000 cycles of a very pronounced effect of that. If you take the same plaques and cycle and you are looking for electrolyte containing lithium, then the cycle life drops off.

And we postulate that the cycle life is not dependent so much on the strength of the plaque, but on the swallowing of active material because of the stress. You simply get stress fatigue of the deposit rather than substrate.

FORD: Thank you. Other questions? Okay, at

this time we will have Dr. Vince Puglisi of Heliotek. The subject is electrochemical impregnation of sintered plaque. The co-authors of this presentation is Dr. Harvey Seiger and Paul Rediman. Dr. Fuglisi?

PUGLISI: At this time I would like to describe Heliotek's effort under Air Force sponsorship in manufacturing electrodes for nickel/cadmium batteries by an electrochemical impregnation technique.

I will first discuss the positive electrode process, then the negative electrode, and finally the program status to date.

On the first slide, I've shown the conditions under which the positive process is presently being conducted at Heliotek.

(Slide 79.)

As one can see, the medium consists of 50 percent ethyl alcohol, nickel and cobalt ion concentrations are 1.8 and .2 molar respectively. The pH of the solution is initially adjusted to a value of less than 2.5 and nitric acid is added during the course of the process to maintain the pH less than 2.5.

The parameters at our disposal can be classified in two groups -- those which remain fixed, where we have arbitrarily or for other reasons decided to fix and those which we vary.

The fixed parameters include the temperature of the bath, which is maintained at 79 degrees Centigrade, concentrations, concentration ratio, et cetera, working electrode, counter electrode spacing, electrode alignment and the material of the counter electrodes, which is nickel 270.

The parameters which we choose to vary include: current density, impregnation times, sinter porosity, and plaque thickness.

On the next slide we show some impregnation data of 78 percent porous, 34 ml. plaque. These are typical types of, typical series of data.

(Slide 80.)

They are grouped according to current density. We used three current densities: .31, .5, and .35 amps per

square inch. The impregnation time ranges as high as 150 minutes. The series three and series four plates constitute two coupon experiments, which I will go into later.

The examples of typical type loadings, which we obtained can be given by entry no. 2, which was a plate loaded at .5 amps for 120 minutes and was loaded to a level of 2.52 grams per cc. of void.

Let me state now that none of these loading levels have been corrected for plate thickening. This plate which was loaded to 2.5 grams per cc. of void exhibited some surface deposition as can be seen in the plate thickening from 34 to 40 mls.

Examples of other types of loadings which can be obtained and the types of thickening are given in entries 5, 6 and 7. These three plates were loaded at .35 amps per square inch for 150 minutes to a level of approximately 2.3 grams per cc. of void with about an average of 2 mls. of thickening of the plates.

May I have the next slide, please?

(Slide 81.)

This is the data tabulated on the previous slide for the series 3 plates. This was a coupon experiment which was carried out in the following manner. The six plates were impregnated at .5 amps per square inch for various periods of time.

We monitored two things: the loading level once the plates were removed as a function of impregnation time and the cell voltage as a function of impregnation time during the course of the process.

As can be seen the loading level curve, which is this curve, rises sharply during the first portion of the experiment and then levels off to a loading level range of about 2.3 grams per cc. of void.

At the same time, during the rising portion of the loading level curve, the cell voltage curve exhibits a plateau. During the bend of the loading level curve, we see a sharp rise in cell potential followed by a second plateau of the cell voltage curve in the region where loading level has levelled off.

We interpret the sharp rise in cell voltage as being indicative of the change in the process. The process is changing from one where loading is occurring in the pores of the plaque to a surface deposition.

And another visible indication of this is the last two plates, or the most heavily loaded plates, has a visible green substance on the surface, whereas the less lightly loaded plates did not have any surface material whatsoever.

May I have the next slide, please?

(Slide 82.)

This is the series 4 plates tabulated in the second slide and, again, here we are applying the same type of data for a coupon experiment, but carried out at .35 amps per square inch.

Here, again, we see that the loading level curve rises sharply, again, bending off and leveling out in the region of about 2.3 grams per cc. of void. If you had noticed the time range of the previous slide that impregnation was in the order of 125 minutes.

The maximum impregnation was carried out to 150 minutes. Again, the interpretation of cell voltage versus impregnation time is the same thing and the same as was the previous slide.

May I have the next slide?

(Slide 83.)

This is the comparison of the two coupon experiments which were carried out at the different current densities. What we have plotted here is loading level versus charge input measured in coulombs.

The upper curve, or the curve exhibiting the higher slope is the curve arrived at using the .5 amps per square inch current density. The lower curve is the one obtained using a current density of .35 amps per square inch.

As can be seen, that for a given charge-input, that the higher current density we get, a higher loading level. However, to achieve the high loading levels in a range of 2.3 grams per cc., the higher current density exhibits a more rapid leveling off and eventually merges into the curve at the lower current density.

ELECTROCHEMICAL IMPREGNATION: $Ni(OH)_2$ / NICKEL ELECTRODES

I. MEDIUM (a) 50% ETHYL ALCOHOL

- (b) 1.8M $Ni(NO_3)_2$
- (c) 0.2M $Co(NO_3)_2$
- (d) pH 2.5

II. PARAMETERS:

FIXED

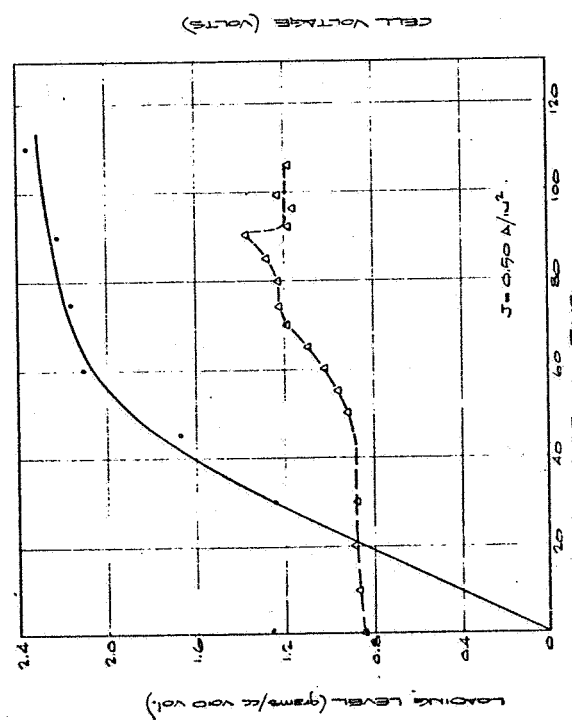
- TEMPERATURE 70°C
- CONCENTRATION'S $Ni/Co = 9$
- FLOW RATE 1.5 gpm
- SEDIMENT VOLUME 4 gal
- WE-CIE. SENSING 0.75"
- ELECTRODE ALIGNMENT
- COUNTER ELECTRODES NTL
- Ni 270

VARIED

- CURRENT DENSITY (j)
- IMPREGNATION TIME
- SINTER POROSITY
- PLAQUE THICKNESS

FIGURE 1

FIGURE 79



LOADING LEVEL VS IMPREGNATION TIME
CELL POTENTIAL VS IMPREGNATION TIME
PLAQUE CHARACTERISTICS: SINTER POROSITY = 75%, PLAQUE THICKNESS 84 MILS.

FIGURE 81

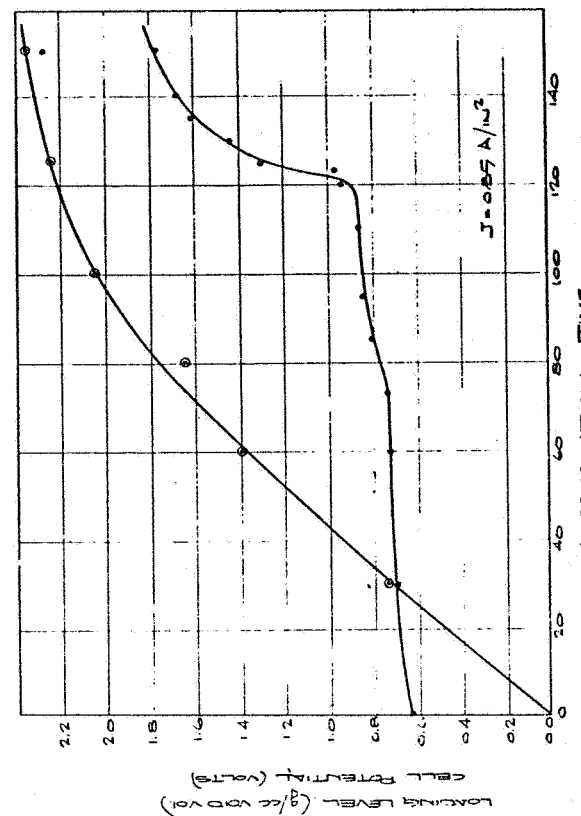
FIGURE 2

ELECTROCHEMICAL IMPREGNATION DATA: $Ni(OH)_2$ / NICKEL

PLATE No.	PLATE SIZE (IN. x IN.)	THICKNESS (MILS) BEFORE AFTER	CURRENT DENSITY (A/IN ²)	IMPREGNATION TIME (MINUTES)	LOADING LEVEL (g/cc void vol.)
1-1	2.0 x 2.5	84.0	0.81	120	2.07
1-2	2.0 x 2.5	84.0	0.81	120	2.02
2	5.0 x 2.5	84.0	0.50	120	2.52
3-1	1 x 2.5	83.5	0.50	30	1.27
3-2	1 x 2.5	83.7	0.50	45	1.67
3-3	1 x 2.5	84.0	0.50	60	2.11
3-4	1 x 2.5	84.0	0.50	75	2.16
3-5	1 x 2.5	84.7	0.50	90	2.22
3-6	1 x 2.5	84.0	0.50	110	2.37
4-1	1 x 2.5	83.6	0.35	30	0.74
4-2	1 x 2.5	83.2	0.35	60	1.37
4-3	1 x 2.5	83.8	0.35	80	1.34
4-4	1 x 2.5	84.3	0.35	100	2.05
4-5	1 x 2.5	83.5	0.35	125	2.24
4-6	1 x 2.5	83.7	0.35	150	2.34
5	8.25 x 4.75	85.0	0.35	150	2.26
6	8.25 x 4.75	85.1	0.35	150	2.29
7	8.25 x 4.75	85.4	0.35	150	2.26

* THE NOMINAL PLATE THICKNESS & SINTER POROSITY ARE 84 MILS. & 78% RESPECTIVELY

FIGURE 80



LOADING LEVEL VS IMPREGNATION TIME
CELL POTENTIAL VS IMPREGNATION TIME
PLAQUE CHARACTERISTICS: SINTER POROSITY = 75%, PLAQUE THICKNESS 84 MILS.

FIGURE 82

May I have the next slide, please?

(Slide 84.)

This is some formation data for the more heavily loaded coupon plates from the previous few slides. I have grouped these according to plates which are similarly loaded using the different current densities.

And what we're doing here is comparing plates of various loading level in their formation performance, as well as plates which are loaded using two different current densities.

The first point or the most important point from this graph is the fact that the more heavily loaded plates both blistered. The plates loaded to 2.1 grams per cc. did not blister.

Plates which were loaded to essentially 2 grams per cc. blistered in one case but did not blister in the second case. The plate which was loaded at the higher current density -- plate 3-5 -- did blister, whereas plate 4-5, which was loaded at .35 amps per square inch did not blister, even though it was loaded to the same level as the 3-5 plate.

May I have the next slide, please?

(Slide 85.)

Again, this is all data for 78 percent porous, 34 ml. plaque. Now, this is the formation history of three other plates, plate 5-1, 5-2, and 5-3.

Now, the points of interest here are the utilization figures. These utilizations were measured to a cut-off voltage of .5 volts. Now, if one notices the average utilization of the three plates is 116 percent. This is in flooded formation after 24 cycles.

An interesting fact of these three plates is the fact that these three plates were loaded simultaneously at .35 amps per square inch for 150 minutes to approximately an average of about 2.3 grams per cc. of void with about a 2 ml. thickening.

The plates were arranged in the plane with plates 5-2 and 5-3 being the outside plates and 5-1 being the center plate. Immediately following impregnation there was noticed that there was an edge build-up on the two outside

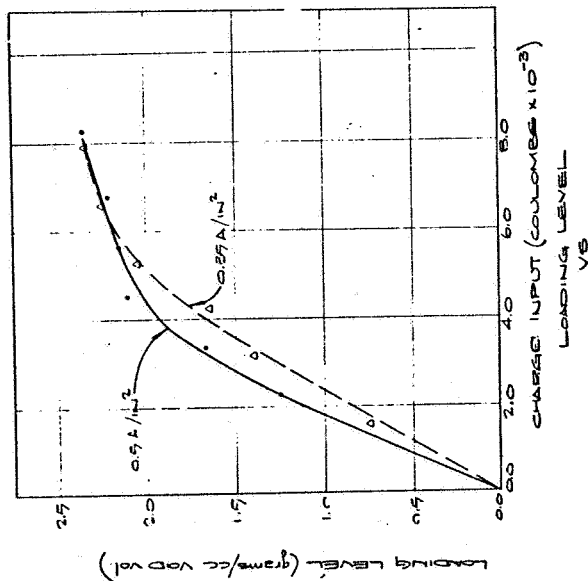


FIGURE 5

FIGURE 83

$\text{Ni}(\text{OH})_2/\text{NIOOH}$ ELECTRODE FORMATION DATA

CYCLE NO.	CHARGE		DISCHARGE		DELIVERED		UTILIZATION %					
	CURRENT (A)	TIME (MIN)	CURRENT (A)	TIME (MIN)	5-1	5-2	5-1	5-2	5-3			
1	6.62	60	3.31	46.1	25.4	1.99	2.92	71	61	80		
2-10 #	2.31	60	2.31	60	60							
11	2.31	60	3.31	92.4	49.9	2.89	2.77	2.76	61	87	88	
12-20	2.31	60	2.31	60	60							
21	2.31	60	3.31	93.9	51.7	2.85	2.86	2.87	83	85	91	
22	5.82	80	2.91	58.9	57.7	2.86	2.84	2.80	78	78	96	
23	5.82	70	2.91	61.9	61.2	59.1	3.00	2.97	2.89	103	110	108
24	5.82	20	2.91	63.4	63.4	60.9	3.09	3.07	2.97	110	119	118

* LOADING LEVEL FOLLOWING ELECTROCHEMICAL IMPREGNATION: 2.42 (7-1), 2.24 (9-2) AND 2.20 (5-3) g/cc void.
 * THE 20% KOH SOLUTION WAS DUMPED & REPLACED WITH FRESH SOLUTION.
 * PLATE NO. 13, THE 1ST, 11TH & 21ST FORMATION CYCLES.
 * ELECTRODES SHOWN IN FORMATION CAN DURING DISCHARGE RESULTING IN PREVENTING CELL FAILURE.
 * TIME FOR CELL TO LEAK TO 0.9 V.
 * FORMATION CYCLES 2-10 & 12-20 WERE NOT MONITORED.
 * BASED ON PLATE WEIGHTS FOLLOWING 24TH CYCLE.

FIGURE 7

FIGURE 85

$\text{Ni}(\text{OH})_2/\text{NIOOH}$ ELECTRODE FORMATION DATA

CYCLE	PLATE No.	BI LOADING LEVEL g/cc VOID	CHARGE CUR. TIME (A) (min)	DISCHARGE CUR. TIME (A) (min)	UTILIZATION (%)	FINAL THICKNESS (mils)
21	8-4	2.16	1.16	86	93.2	99
	4-4	2.05	1.16	86	93.8	105
	3-5*	2.22	1.26	86	96.3	96.0
	4-5	2.24	1.26	86	96.3	84.9
	3-6*	2.35	1.32	86	96.3	85.7
	4-6*	2.35	1.32	86	96.3	85.4
					102	85.5
					98	86.0

FIGURE 6

* SERIES 3 PLATE LOADED AT CURRENT DENSITY = 0.90 A/m²;
 * SERIES 4 PLATE LOADED AT 0.95 A/m²;
 * ELECTROLYTE WAS 30% KOH * PLATES BATTERED DURING FORMATION.

FIGURE 84

plates.

Plate 5-1 did not show this edge build-up. This edge build-up resulted from a non-uniform current density. Now, if I may have the next slide?

(Slide 86.)

What was interesting was the fact that plate 5-2 and 5-3 both blistered, whereas 5-1 did not. And what was additionally of interest was the fact that the blistering pattern followed the edge build-up.

It can be seen here. This slide, although it shows the blistering pattern, does not show the edge build-up which was much more pronounced or visible once the plate had been immediately impregnated.

I think what this tends to say is three things, according to the blistering. One, heavily loaded plates have a higher probability of blistering. Second, it is possible there is a relationship which relates the blistering to the type of current density which is used. And third, conditions which produce areas of higher loading in certain sections of a plate could also produce blistering.

And one example is a non-uniform current density. Other examples could be variation in void volume across a plate, variation in plaque thickness, parameters such as that. I'd like to also add that we have eliminated from our process this occurrence of edge build-up.

May I have the next slide, please?

(Slide 87.)

Here are shown the complete history of 27 plates. These plates were -- the plate characteristics are as follows. The plate was 78.7 percent porous, the initial average plate thickness was 29.3 mls.

These plates were impregnated for 125 minutes at a current density of .35 amps per square inch. The loading level following impregnation was 2.35 plus or minus .07 grams per cc of void. There is no correction here for plate thickening.

The plate thickness or the average plate thickness following impregnation was 29.9 or a plate thickening of .6 mls. Following formation -- and these were subjected to

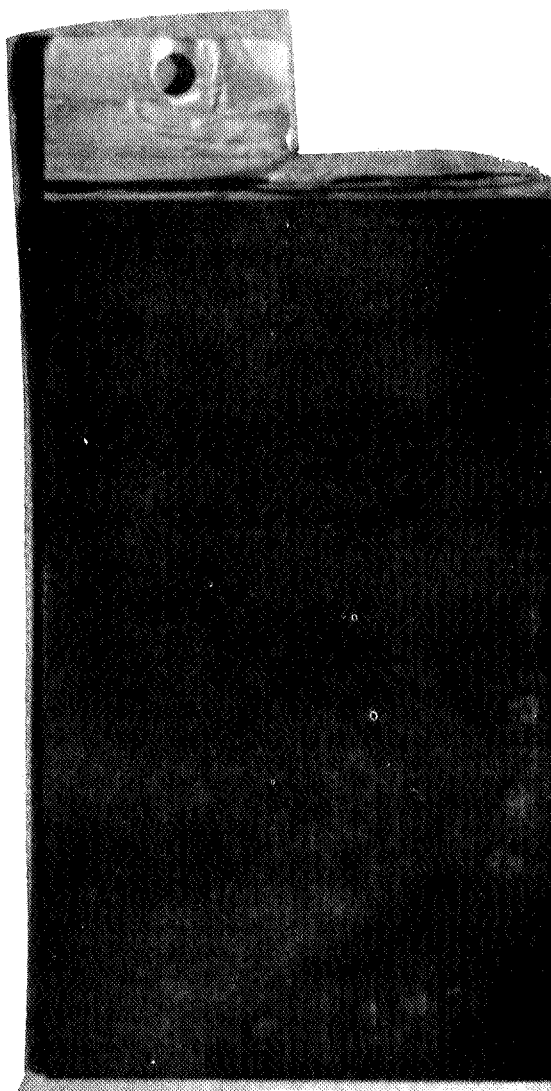


Figure 8
 $\text{Ni}(\text{OH})_2/\text{NiOOH}$ Electrode: Blistering
resulting from edge buildup due
to non-uniform current density.

FIGURE 86

27 formation cycles -- the final loading level of the plate was 1.88 plus or minus .06 grams per cc of void. This value -- 1.88 grams per cc of void -- is, in fact, corrected to plate thickening.

The utilization, measured in the final formation cycle to a voltage cut-off of +0.9 was 109 percent. During the course of the formation, the plates were measured as to thickness and the average thickening was determined after the 14th and after the 27th cycle.

Following the 14th cycle, the plates measured -- an average plate measured 30.6 plus or minus 0.7 mls -- indicating a 1.3 ml. thickening from the initial plaque thickness.

Following the 27th cycle, the plates thickened to a value of 30.8 plus or minus 0.6 mls., an average plate thickening of 1.5 mls. If you were to take this data and plot it versus formation cycles, you would see that plate thickening had increased sharply following impregnation and then levelled off, seemingly levels off as a function of formation cycle and that we're finally looking at an average plate thickening of 1.5 mls.

I'd like to now go to the negative electrode impregnation process and on the next slide I show the medium or the conditions under which the process is presently being conducted.

(Slide 88.)

The medium is entirely aqueous. The solution is 2 molar in cadmium nitrate. The pH is initially set at 3.5 and as Dr. Pickett related, there is no attempt to control the pH during the course of the process.

The parameters which we have at our control include, again, can be classified into those which are fixed and those which are varied.

We operate at a temperature of 101 degrees Centigrade. The concentration is the fixed parameter, cadmium being maintained at 2 molar. The working electrode, counter electrode spacing is set at .75 inches.

Counter electrode material is cadmium and immediately following the impregnation, the impregnated plate is formed in 20 percent KOH, which is maintained at a temperature of 80 degrees Centigrade.

The parameters which we vary in this case include current density, impregnation time, plaque thickness and sinter porosity. There is an additional parameter, which is at our control and that is the technique under which the electrochemical impregnation is carried out.

I'll expand on this on the next slide. We are presently using three techniques to obtain, or we have looked at three techniques to obtain this impregnation.

(Slide 89.)

Method 1 is the constant current step, or which we denote CCS method and in this method -- I apologize to this not appearing -- this is J , the current density. What we do is we apply constant current density for some time -- T_f -- our variable, therefore, are J , the magnitude of the current density, and the time duration in which this is applied.

The second method is an alternating current pulse technique, which we denote ACP. This is similar to the first except that a pulse is applied which is symmetrical with respect to zero current and it is applied for some duration, T_f .

At our disposal are the three parameters -- the magnitude of the current density, the time of the total process, and the frequency of the process, the frequency with which the pulse is applied.

And, in this case, the time of the forward-going pulse, T_c , is equal to the time of the reverse pulse, T_a . The third technique which we have used is an alternating current pulse technique which is assymetric with respect to time. We denote this the ACPT technique.

And this is similar to the second technique in that a pulse is applied. The difference lies in the fact that the time duration that the forward or cathodizing pulse is applied is greater than the time which the reverse pulse is applied -- that is, T_c is greater than T_a .

And so we have an additional variable which we can vary. May I have the next slide?

(Slide 90.)

This shows electrochemical impregnation data of 75 percent porous, 26 ml. plaque. Typical times of impregnation are 12 minutes, current density ranged from about 1.4 amps

$\text{Ni}(\text{OH})_2/\text{NiOOH}$ ELECTRODE IMPREGNATION DATA*

A. PLAQUE CHARACTERISTICS

- ENTER PROPERTY: 18.7%
- INITIAL PLATE THICKNESS: 29.3 ± 0.4
- PLATE AREA: $4.00 \times 2.75 = 11 \text{ in.}^2$
- COINED

B. ELECTROCHEMICAL IMPREGNATION DATA

- LOADING LEVEL*: $2.95 \pm 0.07 \text{ g/cc void}$
- PLATE THICKNESS: 29.9 ± 0.8
- PLATE THICKENING: 0.6 mils.

C. FORMATION DATA

- FINAL LOADING LEVEL*: 1.88 ± 0.06
- FORMATION CYCLE RATE THICKNESS: 30.2 ± 0.7
- UTILIZATION: 109%

PLATE THICKENING
1.3
1.5

- + AVG. OF 27 PLATES
- * DOES NOT TAKE THICKENING INTO ACCOUNT
- * CORRECTED FOR PLATE THICKENING

FIGURE 9

FIGURE 87

ELECTROCHEMICAL IMPREGNATION TECHNIQUES

METHOD CURRENT DENSITY-TIME VARIABLES

A. CONSTANT CURRENT
(STEP) i t x_f

B. ALTERNATING CURRENT
PULSE (ACP) i t_f t_r x_f x_r

C. ALTERNATING CURRENT
PULSE-ASYMMETRIC
WITH RESPECT TO
TIME (ACPT) i t_f t_r x_f x_r

FIGURE 11

FIGURE 90

ELECTROCHEMICAL IMPREGNATION OF SINTERED NICKEL PLAQUE TO MAKE $\text{Cd}/\text{Cd}(\text{OH})_2$ ELECTRODES

A. MEDIUM

- AQUEOUS
- $\text{Cd}(\text{NO}_3)_2$
- $\text{pH} = 5.5$

B. PARAMETERS

FIXED

- TEMPERATURE: 101°C
- CONCENTRATION: $\text{Cd} = 2.0 \text{ M}$
- FLOW RATE: 1.5 gpm
- SOLUTION VOLUME: 4 GAL.
- W.E.-C.E. SPACING: $0.75"$
- ELECTRODE ALIGNMENT: Cd
- COUNTER ELECTRODE MTL.
- FORMATION: 1 20\% KOH
- IMMEDIATELY FOLLOWING IMPREGNATION

VARIED

- CURRENT DENSITY
- IMPREGNATION TIME
- ELECTROCHEMICAL IMPREGNATION TECHNIQUE
- SINTER PROPERTY
- PLAQUE THICKNESS

FIGURE 10

FIGURE 88

ELECTROCHEMICAL IMPREGNATION OF 75% POROUS SINTERED NICKEL PLAQUE* TO MAKE $\text{Cd}/\text{Cd}(\text{OH})_2$ ELECTRODES*					
PLATE No.	ELECTROCHEMICAL IMPREGNATION TIME (MIN)	CURRENT DENSITY ($\text{A}/\text{in.}^2$)	LOADING LEVEL (g/cc void)	LOADING THICKENING (mil)	
2	12	1.4	1.87	0	
4	12	1.6	1.77	0	
8	12	1.8	1.93	0	
6-1	3	2.0	1.28	0.0	
6-2	7	2.0	1.42	0.1	
6-3	7	2.0	1.73	0.0	
6-4	9	2.0	1.80	0.3	
6-5	11	2.0	1.89	0.0	
6-6	13	2.0	2.02	0.3	
6-7	15	2.0	1.95	0.6	
11	12	2.0	0.19	-1.9	
12	12	2.0	0.29	-0.2	
13	12	2.0	0.08	-1.3	
14	12	2.0	1.01	-0.6	
15	12	2.0	1.65	-0.2	
16	12	2.0	0.29	-0.1	
17	12	2.0	0.46	-1.3	
18	24	2.0	0.25	-0.2	

FIGURE 12

FIGURE 89

1202

per square inch to 2 amps per square inch.

The data is grouped according to the electrochemical impregnation technique. The first three entries, entry 2, 4 and 3, which exhibit an impregnation time of 12 minutes at various current densities using the CCS method, yield, illustrate the type of loading levels which are obtained at 0 plate thickening.

We obtained loading levels which range anywhere from 1.8 to about 1.9 grams per cc. of void in a 12 minute time span. The series 6 plates, which were also loaded using the CCS method for various times is another coupon experiment, which I will show on the next slide.

Could I still have that slide please?

The final grouping is a group of plates which were loaded using the ACP technique or alternating current pulse technique for a constant time of 12 minutes and using the current density of 2 amps per square inch.

As one can see from the data, there appears to be a very definite dependence on frequency, that is, the maximum loading 1.65 grams per cc. of void is obtained at 100 cycles per second at frequencies on either side of this frequency, the loading level drops off dramatically.

And in no case is the loading level similar to the loading levels obtained by just this new application of a constant current. Also what's noticeable here is the fact that plate disintegration has occurred in most instances, in every instance.

In an attempt to increase the loading by extending the time but using the optimum frequency, we extended the time of impregnation 24 minutes, kept the current density the same at two amps per square inch resulted in the poorly loaded plate.

Now, may I have the next slide?

(Slide 91.)

This is, again, of the series 6 plates, which were tabulated on the previous slide. It illustrates loading level as a function of impregnation time -- the time duration

approximately 15 minutes for the completion of the process. And, again, this is an experiment where six plates were loaded to various, for various periods of time, at a current density of 2 amps per square inch.

As one can see, the loading level rises sharply and then there's a long portion of the time for approximately three minutes on that the slope of greatly reduced.

We eventually get to a level of about 2 grams per cc. of void. These plates, again, were loaded by the constant current step method. May I have the next slide?

(Slide 92.)

This data here is the impregnation of 82 percent porous plaque, measuring 25 mls. Again, the grouping is according to the technique which was used to affect the loading.

The first series of plates were loaded using the constant current step method. Entry M-2, again, using the CCS method, impregnated for 12 minutes at a current density of 1.6 amps per square inch, resulted in a loading level of 2.18 grams per cc. of void with zero plate thickening.

Extension of the time, as shown in entry M-4, an additional two minutes at the same current density, resulted in a loading level in excess of three grams per cc. of void but with considerable surface deposition. The plate thickened 7 mls.

An attempt to see what type of loadings could be obtained with this porosity plaque using the alternating current pulse technique at 100 cycles per second, which was the optimum frequency determined for the 75 percent porous plaque, resulted in a poorly loaded plate plus considerable plate disintegration.

Two other frequencies were looked at and they also resulted in poorly loaded plates, although at 75 cycles per second, we obtain a loading of approximately 1 gram per cc. of void. This data would indicate to us that although one could obtain fairly reasonable loading levels using an alternating current pulse technique by optimizing the conditions of frequency, current, density, time, et cetera, one could not simply extend those optimized values to a plaque of differing characteristics.

For if one had a 75 percent porous plaque, optimize the conditions under which one would obtain maximum loading, one could not just then extend those conditions to an 82 percent porous plaque.

The final grouping are a group of plates which were loaded using the alternating current pulse technique, which was assymetric with respect to the time axis.

Here, we used an impregnation time of 12 minutes in every case. The current density was 1.6 amps per square inch. The first five entires indicate the type of loading levels which we obtained.

They range from 2.26 grams per cc. of void to 2.35 grams per cc. of void with an average 1 ml. plate thickening. I might point out that the ratio of the forward going pulse to the reverse pulse for all of these experiments or all of the ACPT experiments was maintained at 8 to 1.

Increasing the frequency from 11 cycles per minute to 110 cycles per minute to 1,000 cycles per minute to 11,000 cycles per minute resulted in no great improvement in the loading level, although and neither did it affect the loading level.

Again, we were seeing loading levels on the order of 2.3 to 2.4 grams per cc. of void and the thickness varied somewhat -- usually on the order of from one to two mls.

I'd like to now summarize the program status to date with the information given on the last slide.

(Slide 93.)

The Wright Patterson Air Force contract requirements says the requirement is that the positive electrode is loaded to a level of 1.7 grams per cc. of void. We're presently loading our plaque to 1.9 grams per cc. of void.

We also feel that we know how to optimize the conditions such that for any plaque of any characteristic, we can obtain optimum loading levels. We also feel that the process is well enough understood that we have in fact optimized the conditions.

With the negative electrode, the Wright Pat. contract requirement is that the loading level be 1.6 grams per cc. of void. We are presently loading plaque to at least

SUMMARY: ELECTROCHEMICAL IMPREGNATION TO MAKE
 $\text{Ni}(\text{OH})_2/\text{NiOOH}$ & $\text{Cd}(\text{OH})_2/\text{Cd}$ ELECTRODES

ELECTRODE	LOADING LEVEL (g/cc void)	
	WPAF CONTACT REQUIREMENT	Nov. 73 STATUS
$\text{Ni}(\text{OH})_2/\text{NiOOH}$	1.7	1.9
$\text{Cd}(\text{OH})_2/\text{Cd}$	1.6	1.8

FIGURE 15

FIGURE 93

ELECTROCHEMICAL IMPREGNATION OF 82% POROUS SINTER NICKEL
 PLAQUE* TO MAKE $\text{Cd}/\text{Cd}(\text{OH})_2$ ELECTRODES

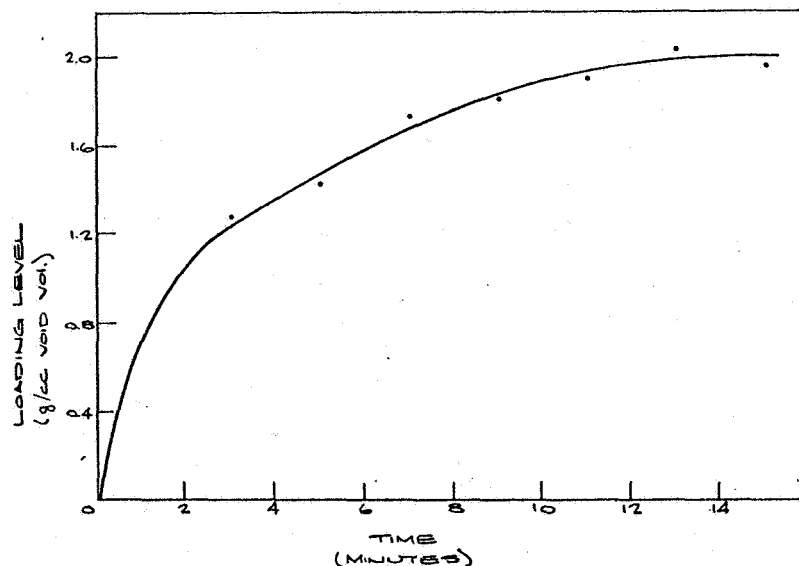
PLATE No.	ELECTROCHEMICAL IMPREGNATION TECHNIQUE	IMPREGNATION TIME (MIN)	CURRENT DENSITY (A/IN ²)	LOADING LEVEL (g/cc void)	THICKNESS (mil.)
M-11	CCS	13.5	1.7	2.00	0
M-2	CCS	12	1.6	2.18	0
M-4	CCS	14	1.6	3.14	7
M-5	CCS	12	1.7	1.99	0
M-3	CCS	12	1.8	2.78	4
M-1*	CCS	12	2.0	1.92	-1
M-7	ACP-100 CPS	12	1.6	2.05	-3
M-9	ACP-75 CPS	12	1.6	0.99	-1
M-10	ACP-50 CPS	12	1.6	2.05	-1
M-12	ACPT-1100 PM-8:1	12	1.6	2.35	1
M-21	ACPT-1100 PM-8:1	12	1.6	2.27	1
M-24	ACPT-1100 PM-8:1	12	1.6	2.26	0
M-25	ACPT-1100 PM-8:1	12	1.6	2.32	2
M-26	ACPT-1100 PM-8:1	12	1.6	2.31	1
M-14	ACPT-1100 PM-8:1	12	1.6	2.49	2
M-16	ACPT-1100 PM-8:1	12	1.6	2.30	5
M-17	ACPT-11,000 PM-8:1	12	1.6	2.38	9

+ PLAQUE CHARACTERISTICS: MARATHON PLAQUE; SINTER POROSITY:
 82%, 25 mil. THICK, $V=0.290$ cc void/in² PLAQUE.

* SCRUBBING REMOVED SINTER

FIGURE 14

FIGURE 92



LOADING LEVEL VS TIME

FIGURE 13

FIGURE 91

a level of 1.8 grams per cc. of void. We do not feel, however, in this instance, that we have sufficiently optimized the conditions such that we are seeing the most heaviest loaded plates that can be obtained and that further effort is necessary with the negative plates.

This concludes my talk.

FORD: Thank you, Dr. Puglisi. Okay, we have a question here.

KRAUSE: (Hughes) Dr. Puglisi, Figure 9 shows the plate thickening of -- I guess something less than $1\frac{1}{2}$ mls.

PUGLISI: The average plate thickening was $1\frac{1}{2}$ mls.

KRAUSE: Subsequent to that you made a correction for loading -- revised it down to something like 1.8 grams. What is the nature of the thickening?

PUGLISI: 1.9 -- I'm sorry -- it's 1.88.

KRAUSE: It implies that a thickening, since you are correcting for average loading for cc. void volume, that the thickening is actually resulting in more pores for doing that correction or is there simply a surface deposition?

PUGLISI: No, the thickening has resulted from the cycling. This is following formation and not a thickening. We're considering a clean plate -- a plate which has been scrubbed and cleaned and the thickening that we're looking at is resulted from cycling of the plate.

KRAUSE: What is the nature? Is there actually a stretching of the sinter material?

PUGLISI: No, this is just the normal growth which has been seen in positive plates due to the swelling from the cycling of the plates due to -- as Dr. Seiger tried to allude to in his talk, he considered the fact that you have these stresses within the pores of the plate which result from volume changes due to the density changes in the species which is present.

KRAUSE: Is this, then, an elastic deformation of the plate -- an inelastic deformation?

PUGLISI: Not elastic, inelastic.

MAURER: (Bell Labs) In your cadmium deposition, the least grams of cc. of void is based on the weight gain?

PUGLISI: Yes, following formation in the 20 percent KOH.

MAURER: Have you ever analyzed the plaque for total cadmium?

PUGLISI: No.

MAURER: I think if you analyzed for nickel hydroxide deposit, I think you'll find that there may be a substantial nickel hydroxide deposit there as well which will contribute --

PUGLISI: Nickel or cadmium?

MAURER: Nickel. Corrosion of the plaque it comes from.

PUGLISI: We're looking at several different processes, so in one case, in the constant current technique, we're always applying a cathodic current, so therefore, we're protecting the plaque during the entire impregnation process.

Now, this may be true in the alternating current technique.

MAURER: If you look at your loading as the function of time, one could extrapolate the data points back to zero time and get a finite loading indicating that you're getting something -- a linear region of loading versus time and then a non-linear component superimposed on it.

I think if you analyze the active material, you'll find that some of it is nickel.

PUGLISI: I think Dr. Seiger would like to comment on that.

SEIGER: The first comment is that the solutions have no green. As long as they have no green, we can't presume that there's no corrosion.

KROGER: That's not correct.

SEIGER: The form of the curve doesn't appear to be linear. It looks like there's an x potential in it. I just forgot what the third point was. When I think of it -- oh, yes, the utilizations that we're getting is something that range in the order of 80 percent, 88 percent,

78 percent, so I don't think we're too far off, assuming that we have no corrosion.

FORD: Dr. Kroger?

KROGER: A sizeable corrosion was current. You will be surprised if you analyze it how much corroded nickel you will find, which I agree -- your argument -- the solution stays clear, does not present the corrosion that stays inside. You'd better look into it.

SEIGER: I have a problem because it's in essence solution and nickel in an essence solution --

KROGER: Not inside the core. You have corrosion occurring inside the plate. It's not necessary that the nickel comes outside. Depending upon your condition you can have corrosion of the nickel up to 20 percent.

SEIGER: I'll have to ask a question then of Dr. Maurer. I never looked inside at corrosion -- I remember a report coming from Bell Telephone Laboratories in which you specifically went at the corrosion point and could produce some experimental evidence by reducing nickel electrodes, that there was no corrosion.

MAURER: That's right.

(Laughter.)

We'll tell you how that's done in a short while, as soon as we are ready, or we have clearance to talk about that.

BOGNER: You studied material utilization as a function of loading?

PUGLISI: On which -- on the negatives or the positives?

BOGNER: Either one.

PUGLISI: Not over wide ranges, no.

SEIGER: It's the preliminary information that we have that it depends upon the porosity of plaque and the degree of loading. The more porous it is, the greater utilization. That's very early data.

DUNLOP: On your matter that you present on the positive electrodes, you show a 27 cycles, you show corresponding utilization increase continuously. It wasn't really clear whether it will ever level off. It got up to about 118 percent from the 27 cycles.

PUGLISI: We know how -- in that particular instance we never did go back and measure an additional cycle. If you recall that data, the plates were removed -- I'll have to look at the slide -- but they were removed and scrubbed.

Let's see that would be seven or eight.

(Slide 85.)

DUNLOP: What happens if you continue the cycle. That is the slide of the 24 figures. You're up to 118. It continue to go up.

PUGLISI: In this particular slide does not show the data. We have other data on similarly loaded plates -- several of them -- where we have taken the plates and cycled them for 24 cycles.

And what we have done is like remove the plates following the 20th cycle, scrubbed the plates and then put the plates back in and then gone ahead and continued the formation -- an additional three cycles.

The changes begin to become random and very up and down depending upon the accuracy of the way the formation is handled, but in that particular case, you're right. The data does not show that it has, in fact, levelled off, but we have other data which does say that it levels off in that utilization range. Okay?

KROGER: I would like to make another point to the corrosion. If I understand you correctly, the weight gain you are observing are in full agreement with utilization?

Don't forget that if you corrode one gram of nickel, you make 1.58 grams of nickel hydroxide, so the error you are making is not that bad. I think you'd better look into it because only half of it or one-third for one nickel that disappears, there's a little bit of weight gain.

All of your corrosion shows up as weight gain, because you have to subtract the weight of the nickel which disappeared. Therefore, your utilization of your negative, active material still may be reasonable although you have a sizeable amount of attack of the structure.

BELOVE: Have you any information on the ampere

hours per cubic inch you are getting on these plates?

PUGLISI: We normally just work in loading levels. I think the data was sufficient, though, you'd probably be able to get those figures out of there.

BELOVE: It's nice to have them, sir, to compare with other values we have seen in the past.

PUGLISI: Our goal in this is a loading level and a 20 watt hour per pound battery.

BELOVE: That's your goal?

PUGLISI: Yes.

FORD: Other questions or comments? Discussion? Okay. Thank you, Dr. Puglisi. Okay, at this time Dr. Scott had some comment he would like to make relative to the merits of coining of sintered nickel plate. I'd like to have Dr. Scott just come up and while he's doing that, I think this will probably be the last paper.

I believe the latest word is they scheduled to have the cocktail party here in this room.

A VOICE: It's room 200 now -- for the floating cocktail party.

(Laughter.)

FORD: Well, that's the third place we've been scheduled to have it. Okay, but nevertheless, it's in this building, so we won't have to leave the building. Room 200 is right down the hall to your left here.

SCOTT: I think it's been generally agreed in principle, at least, among users of nickel/cadmium cells for long life applications that coining of sintered plates is always better than not coining.

I note that the original version of the interim high-rel spec for nickel/cadmium cells dated 1969 has a requirement in there for all plates to be coined. However, in recent times, a number of cell suppliers have apparently taken issue with this and claim that coining is not necessary.

So in order to shed a little more light on the subject, TRW has been awarded a contract to look into this

situation by Jet Propulsion Laboratory. This contract is under the general technical surveillance of Aiji Uchiyama, with Gordon Juvinall there as the Contract Monitor.

And the objective of the work is to sort of look at the state of the art and make an independant assessment, if possible, as to the relative merits of coining versus non-coining, primarily for long-life space applications.

I believe the first viewgraph -- you'll have to excuse the faint print -- the process went out of control a little bit.

(Slide 94.)

To summarize the tasks that we are addressing ourselves to in this study -- to take a look at the state of the art of coining and other edge finishing methods used for nickel/cadmium sintered plates primarily, to obtain coined plate materials and to characterize them, to determine the comparative potential for mechanical damage during, primarily during handling and cell assembly for non-coined and coined edges, to perform a vibration and shock testing of plates in simulated cell configurations.

These shock and vibration levels are typical of that experienced in spacecraft -- to develop and apply an accelerated electrochemical test, to promote edge damage for comparative purposes, to perform accelerated cycle testing of plates in actual cell configurations and to correlate mechanical and electrochemical edge affects with physical and chemical characteristics of the plates.

We're about halfway along on this contract right now. Some of these tasks are completed and others are in the middle and some of them are not started yet. We have made a survey of the industry and are in the process of summarizing what we found.

I won't go into that today. By the way, they're -- an interim report on this project is imminent. It should be distributed next week. We have obtained sample plate materials from quite a few different sources, from companies that wished to participate in this effort.

Some of the information that I'll present will show some of the characterization data from these different plate materials. We have at least tentatively arrived at an accelerated test method that rapidly

promotes edge damage to the edges of sintered plate materials and I'll show you some of the results we have obtained from that.

We haven't started the vibration and shock testing. as yet and we have yet to do the testing in actual cell configurations. All of our testing to date has been in the flooded condition of unsupported plates.

And I'd like to go on to show you some of the results of the characterization tests that we have run. The next slide shows some data from measuring the uncompressed, or uncoined thickness, then measuring the coined thickness and calculating what's referred to as the thickness reduction, which is the difference between coined and uncoined thickness divided by the uncoined thickness in percent.

(Slide 95.)

The different sources are labelled by letters here.

I don't really want to dwell on the actual suppliers. The thing that is interesting is the wide range of values of thickness reduction used by different suppliers.

This slide shows only data for positive plaque, for the finished positive plates and the finished negative plates. Note the range for positive plaque from ten percent to 61 percent.

Similarly on the positive plates, ten percent to 65, negative plates, 17 percent to a maximum of 63.

These differences tend to explain the wide range of opinion and practice with regard to, and actual history

and observations with regard to the effectiveness of coining both during manufacturing process and during life testing where such data on plate material is available.

(Slide 96.)

The next slide shows for four of those six materials or so that were on the previous slide, shows density and void fraction. The density is a pretty direct and simple measurement, I believe.

The void fraction was obtained by uptake of water under vacuum. One of the most interesting things to me is the wide range of values of void fraction in the finished plate materials.

There's some controversy as to the significance of void fraction in a finished plate, but we chose to go ahead and see what we would get.

One of the purposes of coining is to reduce the porosity of the plate material in order that during impregnation it does not pick up as much active material and therefore it is not as active under cycle conditions, and therefore more stable. And, so one of the things that we will expect to do with some of this data is to calculate what the resulting void fraction is in the coined areas and see if that correlates to the results that we get from the testing.

(Slide 97.)

The next slide shows values of what I'm calling relative resistance. Some people refer to it as resistivity, but since I don't know what the current distribution exactly is in these different samples, I think the term "relative resistance" is a little more less presumptive.

The values shown here were obtained by using a four-point contactor, where you supply the current to two

Some manufacturers cut plates before their formations. Some do it afterward. One of the questions that we'd like to address ourselves to is, Is it better to cut before formation or after, or should you cut it at all?

Note the cracking produced by the cut, particularly near the corner.

Some manufacturers have the practice of rounding off this corner after they cut off a plate. Some manufacturers don't -- they just leave the square corner.

Is that good or bad -- I'm not sure, yet, but I have some suspicions.

We're experimenting with some unconventional test methods to get methods of characterizing plate materials that may correlate with the final results that we're getting.

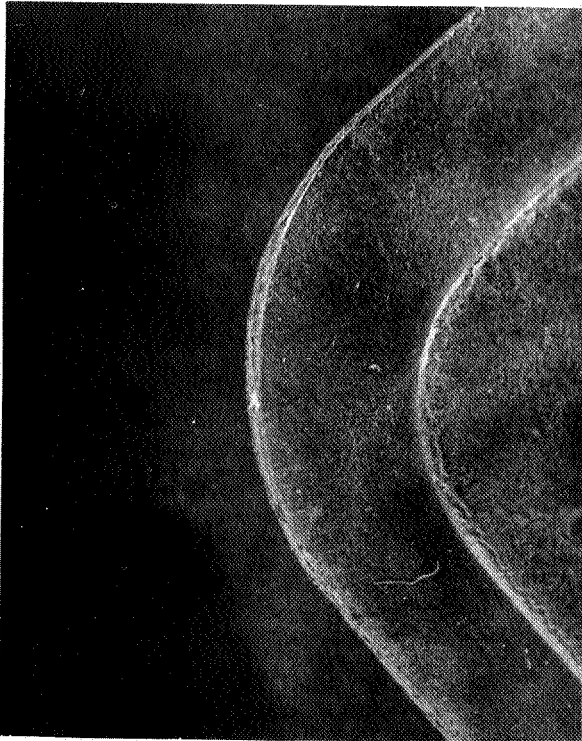
And one of the things that we're interested in is the brittleness and adhesion of the sinter to the substrate. So after doing various things, looking at various methods, we're settled for the moment on a method which involves fairly severe mechanical deformation of the plate by actually bending it around a 3/8 inch polished, stainless steel rod.

The way it's done is the strip of material, say approximately 1/2 inch wide, is cut off a plate and then bent in multiple places over a length of say, like two inches, and then this bent length is then rubbed back and forth over the rod several times -- like shining a shoe -- and the differences that we've seen so far are quite interesting.

(Slide 101.)

This photo represents one of the better plates, one of the better materials. This is a positive plate. As you can see, it's been coined along this upper edge and cut off here.

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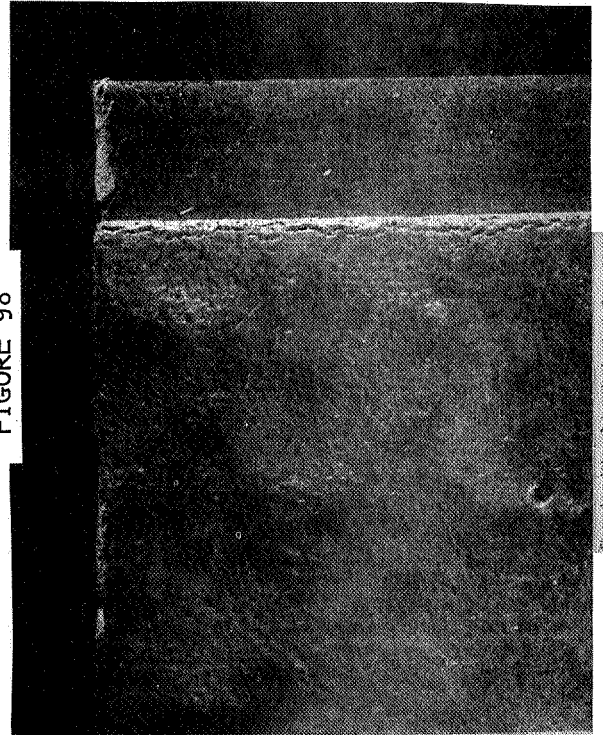
Die-cut, coined corner on a positive plate, showing a smooth, even cut edge (Supplier A)

FIGURE 98



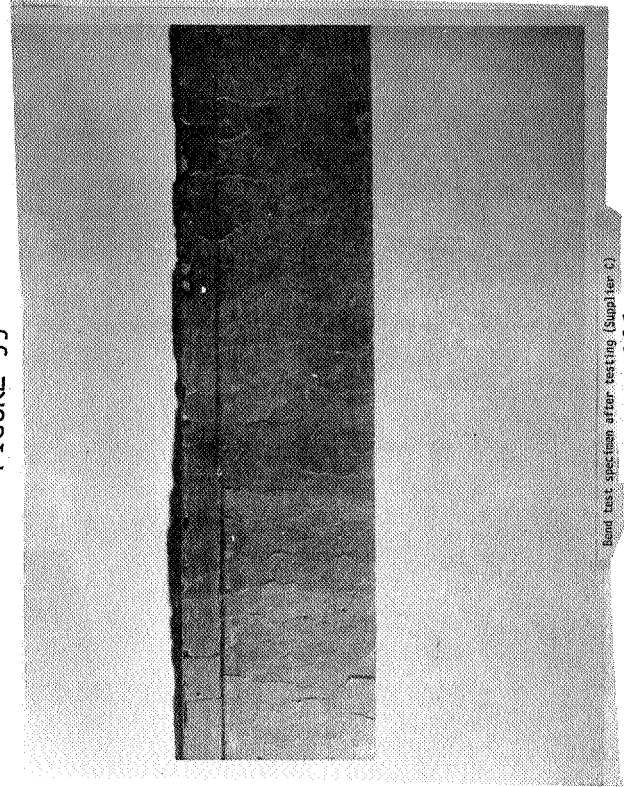
Die-cut, uncoined corner of a positive plate, prior to accelerated electrochemical testing (Supplier B)

FIGURE 99



Sheared positive plate, showing typical cracking along cut edge

FIGURE 100



Bent test specimen after testing (Supplier C)

FIGURE 101

This is one of the better looking specimens after we had performed this test.

(Slide 102.)

The next slide shows one of the not so better specimens. There's obviously a large, significant difference between the brittleness and adhesion of the sinter to the substrate between this sample and the other one.

We're cataloging the different materials with respect to how they show up on this type of test.

The next sequence are some photographs taken of edges of plates that have been put through the accelerated cycling test that I mentioned.

This test, as it now is being done, consists of cycling plates at a current density of two amperes per square decimeter in such a way that each plate is completely charged or discharged on each half-cycle.

When a completely coined plate is tested, at least one of the coined edges is sheared off, so that we have available an uncoined, cut edge to compare with the coined edges.

The charge is taken to the point of rapid gassing in both directions -- that is, in one direction and the opposite direction. The plates are flooded and essentially unsupported. The cycle time is approximately three hours per cycle and the test is carried out usually in the order of 24 hours and then the specimens are examined under the microscope.

During this test, if any sinter falls off, the material collects in the bottom of the container and you can get an idea from that what the total loss of material is.

Now, this is an admittedly severe test, but it appears to show some rather significant differences ranging all the way from pretty good to pretty bad. So it appears to be a useful screening test for the time being.

(Slide 103.)

This is a photograph of a well-coined and die-cut edge after this test. That edge is in pretty good shape. The thickness reduction for this material is about 40 percent, which is about mid-way between the range of values observed for all different materials.

(Slide 104.)

The next photograph shows a portion of that same plate but where the coining had been cut off to expose an uncoined cut edge. Not much edge damage appears to have occurred in the area in the photograph.

(Slide 105.)

The next slide shows a close-up of a similarly cut edge from the same type of plate, after testing. This edge looks in worse shape here. You have some loss of sinter material here and a general roughening of the surface. Thus there is considerable variety even between plates from the same source.

Next slide?

(Slide 106.)

I showed you a while ago a typical uncoined, die-cut corner. (See Slide 99.) This is that same plate after going through this test. Note the severe damage to the edge.

Next slide, please?

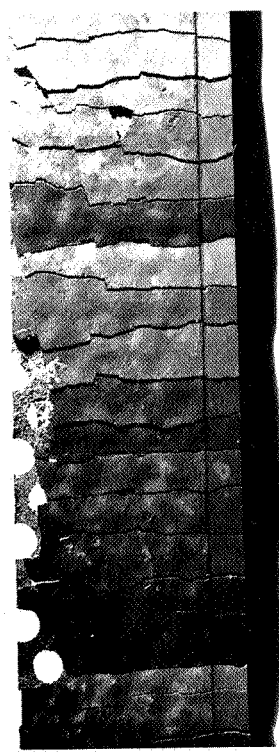
(Slide 107.)

This is, I think, one of the most interesting ones that I have to show. This is a photograph of the top edge of a plate which, if you'll notice here, has been coined.

I think people have noticed, oftentimes -- and I think that Floyd mentioned earlier today -- that a fairly high percentage of cells that show some edge damage tend to show damage across the top edge of the plate.

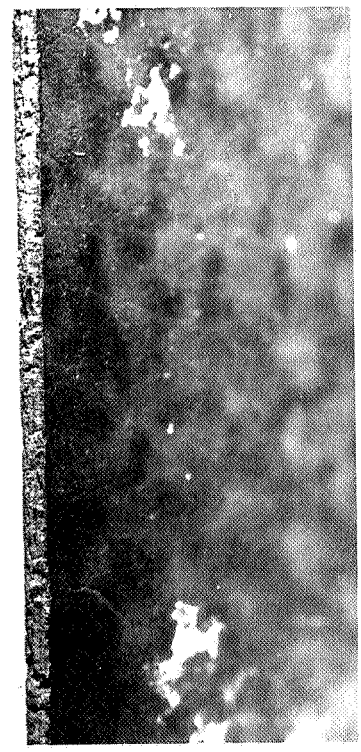
Sometimes it occurs as blistering. In this case, it occurred as disruption of the sinter, right along the very tip edge. Note that there appears to be a fairly

102



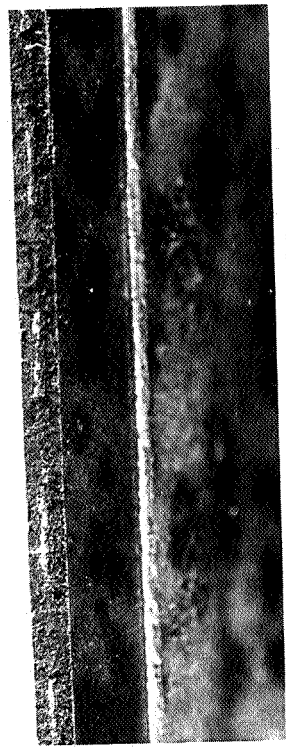
Bend test specimen after testing (Supplier A)
FIGURE 102

104



Beveled, beveled edge of a positive plate, showing a clean cut produced by a sharp, well adjusted tool, prior to accelerated electrochemical testing (Supplier A)
FIGURE 104

103



Beveled edge along the side of a positive plate, prior to (and after) accelerated electrochemical testing (Supplier A)
FIGURE 103

105



Beveled edge, as shown in Figure 7, after accelerated electrochemical testing, showing swelling and pitting (Supplier A)
FIGURE 105

even line right along here extending relatively straight across where the damage appears to have stopped.

So, here we have a case of an apparently coined edge which behaved altogether differently than the other coined edges that we looked at. This was on the same type of plate on which we saw a coined edge that looked in very good condition.

In taking a closer look, it turns out that even though this top edge is "coined", the leading edge is not coined, in fact, because it is tapered. Because this is the very edge of the sintered area of the plate, there is a taper to the sinter and when that original taper thickness gets down to being less than the coined thickness, that part of the sinter is not compressed.

Thus, we have here a situation where the inner part of the coined border is compressed and is therefore strengthened and protected; and then we have a leading edge, which is really not, in fact, coined and so the attack occurs along that area which is representative of uncoined material.

Now, there's a number of ramifications of this. It turns out that on this same plate and on others, if you look at this same situation on the tab, where there is a taper, you don't see this damage occurring.

Apparently, what's happened here is that in trimming off the very tip edge of this tapered and uncompressed material, possibly the very edge has been cut off and exposed and is able to absorb electrolyte and produce a different effect than you get when you don't cut off the feather edge of that coining.

(Slide 108.)

The next slide shows some additional photographs that were taken of edges of plates to get a better idea of what the taper looks like. Here you see an edge-on view of a plate looking at the plate from the edge nearest the tab.

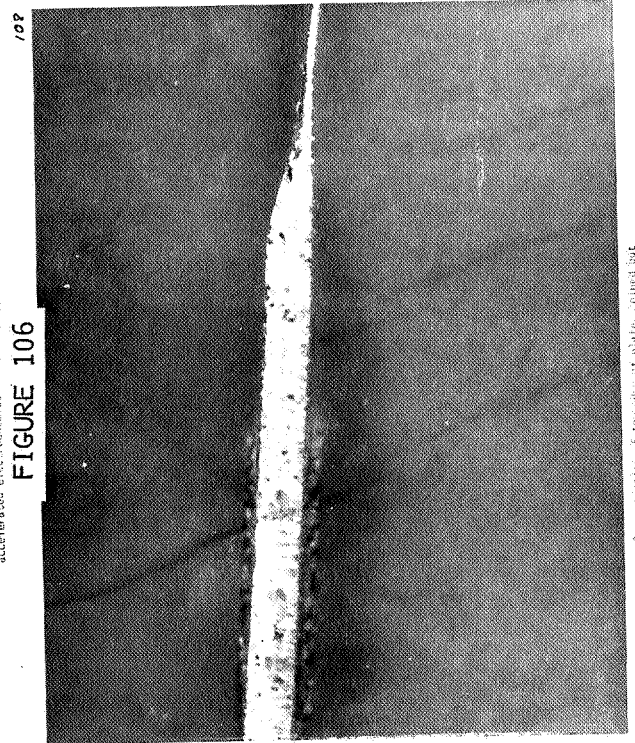
You can see the original uncoined thickness here and you can see the thickness of the coined edge running all along this side and here you can see this big taper up here which, if you look at the face view, it looks like it is coined. But, indeed, it is not in the tapered region..

(Slide 109.)



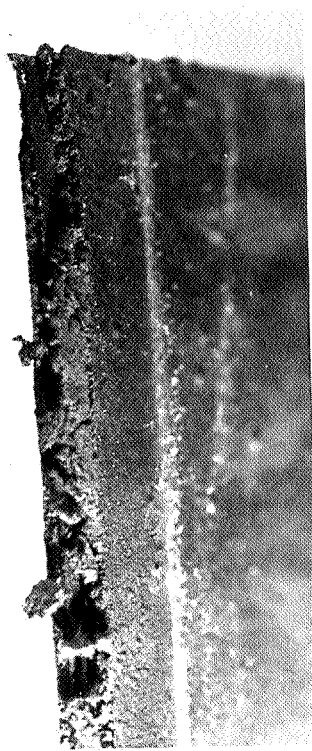
Corner of positive plate, as shown in Figure 3, after accelerated electrochemical testing (Supplier B)

FIGURE 106



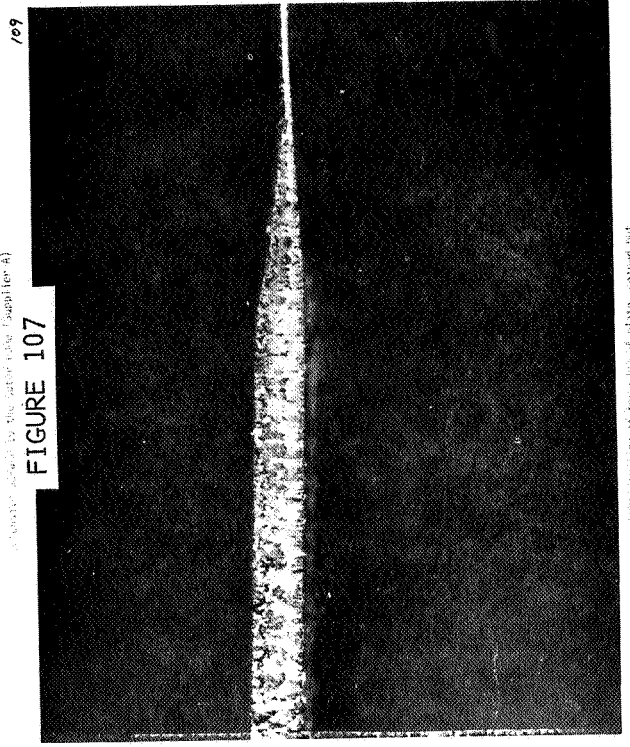
Cross-section of the corner of plates joined but uncut, showing residual layer at outer edge (Supplier B)

FIGURE 108



Sheared edge along the top of a positive plate, after accelerated electrochemical testing, showing a rough surface to the outer edge (Supplier A)

FIGURE 107



Cross-section of top edge of plates joined but uncut, showing residual layer at outer edge (Supplier A)

FIGURE 109

The next slide is a similar view of a plate from a different source where we have an even longer, skinnier taper. This makes it even more difficult to properly compress the very top end of that plate material to obtain the benefits of coining.

Here, again, you can see, somewhat out of focus, the original uncoined thickness of the plate in the background.

The next slide?

(Slide 110.)

Here is an edge view, looking down the edge of a plate from the side opposite that of the tab. The tab is back here out of focus. You can see here where the top edge of this plate was trimmed off. Thus, they happened to have trimmed it down to the point where almost no tapered material is left. This is probably going to be a pretty good coining job at the top end and not experience any damage.

(Slide 111.)

This is an end-on view of the top edge of another plate which shows the coining at the top in profile, where the coining shoulder is here -- the uncoined area is back here and you see the top end has been cut off during the normal die-cutting of the plate.

LANDER: May I ask a question before you go on? Is that black area we're looking at just before the shoulder a void? It looks like it could be a void.

SCOTT: I can't remember right now, John. You know, there are some color differences along these edges that tend to be confusing. I just don't remember in that case.

Thus, there appears to be a considerable variation in the registration between coining and the final die-cutting of the plates. Since that variation all seems to occur in this tapered area, it looks like that can introduce a large variation in the susceptibility of the top edge of the plate to damage under cycling conditions. So this is something which needs to be nailed down in the terms of process control.

Do you have any more, or is that the last one?



Cross-section of top edge of plate, coined and cut, showing removal of tapered edge

FIGURE 110



Cross-section of top edge of plate, coined and cut, showing incomplete removal of tapered edge

FIGURE 111

137a

A VOICE: That's the last one.

SCOTT: Okay, I guess that's all that I have to say.

FORD: Okay. Questions?

HENDEE: First of all, I wondered if you noticed any kind of deterioration in the crack that forms in the interface.

SCOTT: First of all, we have just gotten our toe into the water, and so the number of tests we have run so far is relatively small. And, you know, I don't know how representative exactly any remark I might have to make at the moment is going to turn out to be.

However, so far we have not seen any effect at that crack along the shoulder. I believe what happens is that that crack forms -- of course, you may or may not be aware that, in general at least, I believe that all these plates are coined prior to impregnation, so that crack occurs in the unpregnated material, excuse me.

During impregnation that crack gets coated, filled, cemented with active material. So it does not behave like a crack which forms after impregnation, and so it is a crack of a different nature than those that may form by cutting and flexing and damaging a plate after formation. So, I would not expect that crack to behave the same way.

HENDEE: I know certain companies reject any plaques prior to impregnation formation on what appear to be maybe that size. I was just wondering if you have seen deterioration in that. What I was really aiming at, have you considered any kind of a tapered plane?

SCOTT: We are considering variations on the normal form of coining, and we did ask a number of manufacturers whether they were aware of or had used other shapes and types of coining. There wasn't much information available.

There was a general feeling that, yes, there are probably better ways of coining than are being used right now, but not much opinion other than that.

FORD: Stan Krause.

KRAUSE: I know of at least one manufacturer who has assembled probably thousands of cells which have been

flown and tested and cut to edges of their plates. I was wondering if you could give me an idea what the value rates of these cells have been with regard to edge degradation.

SCOTT: No, offhand I could not. I feel that there have been probably quite a few shorting failures that have resulted from this cause that have remained unidentified because of the problems of destroying evidence when cells are taken apart.

But I couldn't really say, other than that. The approach that we are taking here is looking at very long life, very high reliability applications, where we can't very well predict the effect of time. And so, you know, we just want to get a better handle on some of the more obvious problems that might be encountered.

FORD: Just one comment, Stan. I mentioned earlier the first cell failure that occurred in the real time synchronous orbit test at Crane, and that was like after four and a half to five years, was attributed to the destruction of the positive plate around the tab area, around the coined area up at the top of the plate and on the plate edges that were cut.

Which one caused the cell to short wasn't known, but both areas looked very bad, and I would be glad to show you those photographs if you would like to see them at a later time.

I hate to cut this short, but the cocktail hour was supposed to start at a quarter of six, and the people are waiting for us. If you will just follow the guys right around the hallway, 200 is straight across from us here.

And we will see you in the morning at 9 o'clock. We have a lot of material to cover, so I ask you to please be prompt, because we are going to get started sharply at 9.

(Whereupon, at 6:05 p.m., the proceedings were recessed to reconvene at 9 a.m. the next day.)

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